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THE CRYSTAL STRUCTURE DETERMINATIONS OF

WILKINSON'S CATALYST AND ITS DIOXYGEN DERIVATIVES

by

Ⓒ PETER BLAIR DONALDSON

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and
recommend to the Faculty of Graduate Studies and Research,
for acceptance, a thesis entitled ..The.Crystal........
Structure.Determinations.of.Wilkinson's.Catalyst.and.its
Dioxygen.Derivatives...................................
submitted by ..Peter.Blair.Donaldson...................
in partial fulfilment of the requirements for the degree
of Doctor of Philosophy.

Abstract

A brief chemical introduction is given which
includes short discussions of the principles of oxidative
addition, the history of the solution studies performed
on *tris*-triphenylphosphinechlororhodium(I) - known as
Wilkinson's catalyst, and types of dioxygen coordination.

The dioxygen derivatives of the above complex
and its iodo analogue were synthesized. The crystal and
molecular structures of the red and orange modifications
of the catalyst and its *bis* and *tris*-triphenylphosphine
dioxygen derivatives were determined.

The *bis*-phosphine dioxygen complex crystallizes
in the space group $P\bar{1}$ (a, 13.889(7); b, 13.678(6); c,
11.433(5) $\overset{\circ}{A}$; α, 105.73(4); β, 115.74(3); γ, 100.97(4)°)
with 1 molecule per unit cell (ρ_{obs}, 1.470; ρ_{calc}, 1.469
g-cm^{-3}). The model converged to a final R factor of 0.044.
The complex is a dimeric species with dioxygen molecules
bridging the rhodium atoms in a novel manner.

The *tris*-phosphine complex crystallizes in the
space group Pbca with 8 molecules per unit cell (ρ_{obs},
1.411; ρ_{calc}, 1.416 g-cm^{-3}). The axial parameters are:
a, 24.817(4); b, 18.359(2); c, 23.200(4) $\overset{\circ}{A}$. The refine-
ment converged at R = 0.049. The molecule contains a
π-bonded dioxygen ligand with additional hydrogen bonding
being evident. A discussion of the dioxygen bonding in

both derivatives is included.

The orange allotrope of $RhCl(P(C_6H_5)_3)_3$ crystallizes in the space group $Pna2_1$ (a, 19.470(3); b, 12.689(2); c, 18.202(3) Å) with 4 molecules per unit cell (ρ_{obs}, 1.363; ρ_{calc}, 1.367 g-cm^{-3}). The refinement converged at a conventional R factor of 0.047. The complex has a square planar central geometry with a small approximately tetrahedral distortion.

The red modification of $RhCl(P(C_6H_5)_3)_3$ crystallizes in the space group $Pna2_1$ (a, 32.96(1); b, 12.271(2); c, 11.013 g-cm^{-3}) with 4 molecules per unit cell (ρ_{obs}, 1.382; ρ_{calc}, 1.379 g-cm^{-3}). The refinement converged at R = 0.042. The complex has a more distorted central geometry than the orange form. Variations in the rhodium-phosphorus and phosphorus-carbon bond lengths within the same species are discussed and comparisons drawn between the two forms of the catalyst and the two dioxygen derivatives.

Two very brief appendices are included and give explanations of computer programmes used and symbols not defined in the text.

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CHAPTER I

Chemical Introduction

Transition metal complexes are known to be
very reactive in promoting chemical reactions and play
an important role in the transport of molecular oxygen.
One such complex, $RhC\ell(P(C_6H_5)_3)_3$ [1,2], acts as a homo-
geneous catalyst in a number of chemical reactions [3]
and binds molecular oxygen. It was extensively studied
when the research described in this thesis was initiated.
The following points are important when considering
homogeneous catalysis by this complex: (1) the general
principles of oxidative addition, (2) the history of
the solution studies of $RhC\ell(P(C_6H_5)_3)_3$ and (3) the
types of dioxygen coordination in transition metal
complexes. These topics will be briefly presented in
this chemical introduction.

A number of publications have appeared dealing
with transition metal complexes that react in a catalytic
manner and these have been classified as proceeding by
mechanisms such as oxidative addition [4,5,6], insertion [7],
ligand exchange [8] and reactions with Lewis acids or
bases [9]. Attempts have also been made to outline the
fundamentals of catalysis more generally [10,11], however
no scheme has been presented, except perhaps the 16 and

18 electron rule [12], which relates the different reaction types or permits mechanistic predictions.

Principles of Oxidative Addition

The term oxidative addition has been used to describe a large variety of reactions in which an increase in the oxidation number of the metal is accompanied by an increase in the metal coordination number. The oxidation number is designated following the accepted convention of assigning to the ligands in the complex the shared electron pairs which constitute the metal-ligand σ-bonds. A typical reaction of this type is the hydrogenation of Vaska's compound [13,14] depicted in equation 1.

$$Ir^{(I)}(CO)C\ell(P(C_6H_5)_3)_2 + H_2 \rightarrow Ir^{(III)}(CO)C\ell(P(C_6H_5)_3)_2H_2$$

$$(1)$$
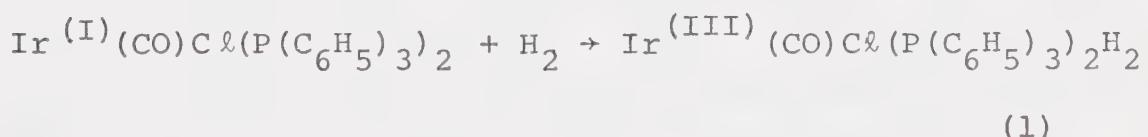
The occurrence of oxidative addition reactions shows an inverse dependence of the preferred coordination number with the d-electron population of the transition metal. This trend illustrates the constraints of the 18 electron (or noble gas) rule where stable configurations of complexes are restricted to those in which the total number of valence electrons (comprising the transition metal d electrons and the σ-bonding electron pairs donated by the ligands) does not exceed 18. Other

stable configurations usually having 16 electrons are
known as coordinatively unsaturated complexes. These
unsaturated complexes undergo a large number of catalytic
reactions and coordinative unsaturation is a prerequisite
for catalysis and usually a prerequisite for a complex
to be able to react by an oxidative addition mechanism.
The closed shell configurations corresponding to 18
valence electrons tend to be particularly stable and
widespread.

Oxidative addition of Vaska's compound could
be represented as [12]

$$ML_4 + L_2 \underset{+2e}{\overset{-2e}{\rightleftarrows}} ML_6 \tag{2}$$

d^8 (16 electrons) d^6 (18 electrons)
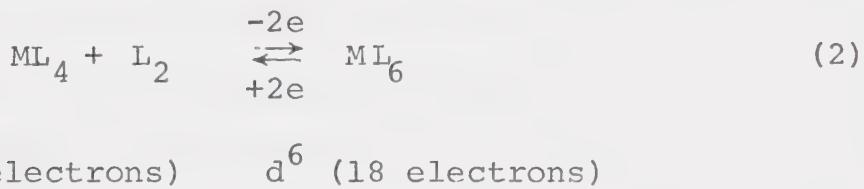
however Vaska *et al.*, [15,16] have shown such a class-
ification proceeding by a two electron step, to be
unrealistic. They found that the concept of integral
oxidation states for the metal did not agree with the
gradual variation in the carbonyl stretching frequencies
as ligands of varying electron accepting abilities
(acidities) were coordinated. These frequencies varied
from 1967 cm^{-1} in the parent d^8 complex, with an
oxidation number of 1.0 to a final value of 2075 cm^{-1}
for chlorine addition, iridium oxidation state 3.0. The

carbonyl stretching frequencies were used to assign
relative oxidation states to the metal. It was found
that the addition of ligands was easily reversible to
a relative oxidation state of 2.24, stable but still
reversible from 2.46 to 2.85 and stable irreversible
from 2.85 to 3.0. The complex $RhC\ell(P(C_6H_5)_3)_3$ has no
such convenient spectroscopic feature and structural
studies are required to furnish similar information.

Oxidative addition reactions of these complexes
should not be considered as integral donations of
electrons from the metal to the incoming ligand, the
coordination number being increased simultaneously, but
rather as a gradual sharing of charge depending upon the
electronegativity of the new ligand. Ligands accepting
only small amounts of charge would not be expected to
coordinate strongly or, if diatomic molecules, they would
not be particularly perturbed by such donation. Con-
versely ligands such as $C\ell_2$ accepting large amounts of
charge from the metal would be highly perturbed by this
charge addition, strongly bound and the original diatomic
structure destroyed. Other evidence to support this
includes the structural data on dioxygen derivatives of
Vaska's compound [17,18,19] and its analogues [20], where
it was found that the greater the perturbation of the
dioxygen molecule (as indicated by the increase in the

oxygen-oxygen distance), the more irreversible was the oxygenation. $(O_2)Ir(CO)Cl(P(C_6H_5)_3)_2$ has an oxygen-oxygen distance of 1.30(3) Å compared to 1.51(3) Å in the iodo analogue. The first complex can be deoxygenated, whereas the second cannot. This trend was also reflected in the structure of the complex $(O_2)Ir((C_6H_5)_2 - PCH_2CH_2P(C_6H_5)_2)_2$ where the oxygen-oxygen distance was 1.63(2) Å and again the oxygenation was irreversible. Vaska and a number of other authors have studied the reactions of related iridium and other d^8 complexes with gaseous molecules. The various influences upon reactivity have been separated and studied as follows.

Vaska et al., [21] studied the role of the metal by substituting cobalt and rhodium for iridium in the complex $Ir(2=phos)_2X$, where 2=phos : cis-$(C_6H_5)_2PCH=CHP - (C_6H_5)_2$ and X : Cl^-, I^-, BF_4^-, $B(C_6H_5)_4^-$. Although a number of studies [15,22-24] have been carried out, comparisons had only been made between second and third row transition metal complexes where the usual reactivity order was third row > second row and by assumption also > first row. Vaska et al., found a reactivity order of Co > Ir > Rh. They also noticed that the enthalpies of activation were proportional to the electronic excitation energy of the three complexes and possibly [25,26] to their ligand field stabilization

energies. The initial structure of the complex was also found to be important as $CoCl(P(C_6H_5)_3)_3$, reportedly tetrahedral [27], was relatively inactive to hydrogenation and oxygenation, whereas the more planar rhodium analogue [138] is reported to be reactive [3]. Ibers *et al.*,[20,28] and Amma *et al.*,[29] concluded from structural data on similar complexes that the overlap between the ligand and substrate orbitals was less in rhodium than iridium complexes, owing to the higher energies of the rhodium d orbitals.

Vaska, Chen and Senoff [14] examined the role of the halide and found that the reaction rate was proportional to the basicity of the complex in the series $(O_2)IrA(Co)(P(C_6H_5)_3)_2$; A:F, NCO, $OClO_3$, Cl, I etc. In addition the free energy of activation increased with increasing energy of the electronic transition in four halo complexes. The calculated enthalpy changes for oxygenation were also similar to that for oxymyoglobin [30].

Vaska and Chen [31] compared the rates of oxygenation of $IrCl(CO)(PR_3)_2$ and found that the rate of formation and stability was directly proportional to the basicity of the phosphine ligand. Steric complications [32] were also apparent as *ortho* substituted groups did not undergo oxygenation whilst *meta* and *para* substituted analogues did. Other bulky ligands also appeared to

inhibit the reaction. These effects have been illustrated structurally as the more basic complex $(O_2)Ir(CO)C\ell((C_6H_5)_2(C_2H_5)P)_2$ [33] had a longer oxygen-oxygen bond length (1.46(2) Å) than its less basic analogue $(O_2)Ir(CO)C\ell(P(C_6H_5)_3)_2$, (1.30(3)Å).

Vaska et $al.$, [15,16] and others [34-36] studied the effect caused by changing the incoming covalent molecule and found that the chlorine-iridium-carbon angle varied considerably. They proposed that in keeping with the concept of non-integral metal oxidation states, the geometries could be interpreted as involving fractional coordination numbers of the metal as some structures were clearly intermediate between regular structural types. When the 'acidity' of the incoming molecule was varied, it was found that the greater the acidity, the less reversible and more rapid was the resulting reaction.

Perhaps a better method of comparing these complexes is as a series of compounds either having 16 or 18 electrons depending upon whether the complex is coordinatively unsaturated or saturated. These electrons should not be designated as being specifically associated with either the metal or ligand orbitals but rather as being located in a series of metal-ligand orbitals, the nature of which depend upon the basicity of the initial metal complex and the acidity of the

incoming ligand.

Solution Studies of $RhCl(P(C_6H_5)_3)_3$

The initial publications of Wilkinson *et al.*,[3] and Bennett and Longstaff [1] suggested that $RhCl(P(C_6H_5)_3)_3$ underwent an initial dissociation step with loss of triphenylphosphine upon dissolution. The research mentioned in this thesis was initiated when this was still the accepted viewpoint. If such dissociation did take place then the solution species would either have solvent coordinated to the metal or be coordinatively unsaturated with a minimum of 14 electrons in degassed solutions. In recent years a large amount of research has been directed towards the understanding of the nature of the solution species as it was thought to be highly relevant to the action of $RhCl(P(C_6H_5)_3)_3$ as a homogeneous solution catalyst. In addition if such solution behaviour was correct then there appeared to be inconsistencies between the ostensibly similar compound $Ir(CO)Cl(P(C_6H_5)_3)_2$ and $RhCl(P(C_6H_5)_3)_3$ and the rhodium complex would not react by an analogous oxidative addition mechanism.

Eaton and Stuart [37] studied the ^{31}P NMR of $RhCl(P(C_6H_5)_3)_3$ in $CDCl_3$ and found no peaks of significance associated with free triphenylphosphine. They did however find some evidence of triphenylphosphine oxide and when the concentration of the complex was lowered to 10^{-3} M,

some small peaks possibly representing free triphenyl-
phosphine were observed. They concluded that the degree
of triphenylphosphine dissociation was less than 5% in
solutions with concentrations in excess of 10^{-2} M. In
addition there was no evidence of halide dissociation.
The coordinated triphenylphosphine *cis-trans* splitting
was then studied and the activation energy for *cis-trans*
isomerisation found to be ~6 kcal-mole^{-1}. The rate of
this isomerisation was greater than the rate of ligand
exchange. A simple dissociative mechanism was thus
eliminated as the mechanism of isomerisation. They then
concluded that although the intermediate could have been
a tetrahedral isomer this was not confirmed and the
intermolecular mechanism probably involved a structure
similar to an ion pair intermediate with one of the tri-
phenylphosphine ligands less strongly bound than the
other two. Their study directly contradicted the simple
dissociative mechanism predicted by Wilkinson *et al.*, in
solutions of concentration greater than 10^{-2} M. These
earlier conclusions were based upon osmometric studies
so Eaton and Stuart repeated this work and confirmed
that the molecular weight of the solution species was
approximately 600, thus indicating a *bis*-phosphine complex.
The inconsistency between the NMR and osmometric findings
thus remained.

Augustine and Van Peppen [38] found that the dissociation of $RhCl(P(C_6H_5)_3)_3$ occurred readily in benzene but was completely inhibited by even small amounts of ethanol: their results again being based upon osmometric studies. They also noticed that the amount of oxygen reacting with the complex was quite solvent dependent and postulated the rather unusual species $[(O_2)RhCl(P(C_6H_5)_3)_2]_2O$ as a product. However the analytical results leading to this formulation are far from convincing. The isomerisation of olefins by $RhCl(P(C_6H_5)_3)_3$ was also found [39] to be most dependent upon the presence of oxygen and the solvent used.

Lehman, Shriver and Wharf [40] suggested that although the solutions used in the osmometric studies had all been stated to be degassed, some oxygen may have been present, causing a lowering of the apparent molecular weight. They rigorously excluded air from their experiments and initially added BF_3 to the solution. If free triphenylphosphine was present they should have obtained the complex $(C_6H_5)_3PBF_3$, however no such species was formed. Freezing point studies were then undertaken with the solvents being first distilled under nitrogen, degassed at high vacuum and transferred in a high vacuum line [41,42]. On four determinations in benzene ranging from 2.39×10^{-3} to 5.85×10^{-3} M, they obtained a molecular weight of

950 ± 40 *cf.* 925 for the parent complex. Using 1,2-
dichloroethane the value was ~920 for a 3.22 x 10^{-2} M
solution. A trace of oxygen was then admitted and the
apparent molecular weight in both solutions dropped to
ca. 600 (in agreement with the previous osmometric
results). It thus appeared that these earlier results
were incorrect and that the presence of oxygen was
causing the lowering of the apparent molecular weight. This
was supported by the appearance of triphenylphosphine oxide
peaks in the ^{31}P NMR studies of Eaton and Stuart as this
complex has been shown [43] to be a product from the reaction
of similar homogeneous catalysts with oxygen. The ^{31}P
NMR results were confirmed at similar concentrations by
Shriver et al.

Arai and Halpern [44] then determined the equilib-
rium constant for dissociation spectrophotometrically in
benzene (1.4(± .4) x 10^{-4} M at 25°C) and again supported
the amended conclusions that in more concentrated solution
(in excess of 10^{-2} M), dissociation was not extensive.

The nature of $RhCl(P(C_6H_5)_3)_3$ in benzene and
chlorinated hydrocarbons under inert atmospheres thus
appeared to be settled. As the hydrogenation reactions
involving this complex included an initial interaction
with hydrogen it was necessary to find out whether this
reaction proceeded by a normal oxidative addition

mechanism or involved, as was apparently the case in the oxygenation reaction, expulsion of a triphenylphosphine upon coordination of the gaseous molecule.

Meakin, Jesson and Tolman [45] undertook a UV spectrophotometric study of $RhCl(P(C_6H_5)_3)_3$ with hydrogen in methylene chloride and observed that as the concentration of hydrogen was increased only one isosbestic point was obtained (360 mµ). This indicated the presence of only two chromophoric species in solution. From their additional ^{31}P and ^1H NMR studies they concluded that these species must correspond to the equilibrium:

$$H_2 + RhCl(P(C_6H_5)_3)_3 \rightleftarrows H_2RhCl(P(C_6H_5)_3)_3 \qquad (3)$$

This reaction could then be considered as proceeding by an oxidative addition mechanism. Tolman [12] has proposed a complete mechanism for the hydrogenation of a terminal olefin by $RhCl(P(C_6H_5)_3)_3$ with two paths arising from the possibility of coordinating hydrogen or olefin initially.

Molecular Oxygen Complexes

Molecular orbital theory has given an explanation for the biradical nature of the dioxygen molecule in its ground state [46] ($^3\Sigma$). Table 1 shows the molecular orbital configurations for various states of dioxygen. The excited state $^1\Delta O_2$ is diamagnetic and is located at 23.4 Kcal-mole^{-1} [47] above the groundstate. The other diamagnetic

The other diamagnetic state $^1\Sigma$ with opposing spins
requires even more energy (37.5 kcal-mole^{-1}). The
superoxo ion (O_2^-) and the peroxo ion (O_2^{2-}) should be
paramagnetic and diamagnetic respectively.

The geometries of the dioxygen molecular
orbitals [48,49] are shown in Fig 1 and the oxygen-oxygen
distances in O_2 ($^3\Sigma$), O_2^- and O_2^{2-} have been measured and
are listed in Table 2. As a result coordinated dioxygen
has tended to be classified on its oxygen-oxygen bond
length alone and not by consideration of the geometry
of the coordination between the metal and the dioxygen
molecule. Species such as $(O_2)IrC\ell(CO)(P(C_6H_5)_3)_2$ and
$(O_2)IrI(CO)(P(C_6H_5)_3)_2$ with oxygen-oxygen distances of
1.30(3) and 1.51(2) Å respectively, have thus been
classified initially as containing either a superoxide
or peroxide ion. They should however (as mentioned
earlier) be viewed more realistically as involving dif-
fering degrees of charge transfer from the ligand to the
metal and *vice versa* but not in an integral fashion.
Unfortunately these bondlength classifications have been
extensively used in the discussion of the bonding within
a number of the following dioxygen cobalt complexes (see
Table 4).

Compounds undergoing oxygenation have been of
interest for some time as oxygen transport in biological

systems [50-52] and a number of autoxidation reactions [43-58] are thought to proceed by the formation of an initial oxygenated complex. The first example of a synthetic reversible dioxygen carrying complex was prepared in 1933 [59], when it was found that red-brown crystals of *bis*-salicylaldehyde ethylenediimine cobalt(II) darkened on exposure to air. It was five years before this darkening was attributed to the reaction with molecular oxygen [60]. Much research [47,61-63] has been directed into understanding the nature of this complex and other dioxygen species.

Definitive studies of the structures of dioxygen complexes suggest three major structural categories:

(1)   (11)   (111)
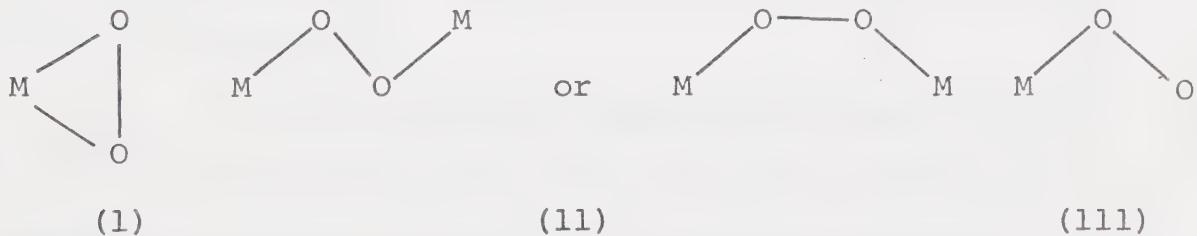
A large number of class (1) complexes have been prepared [47] some of which are represented in Table 3. The bonding in these complexes was first proposed by Griffith [64] and is discussed in later chapters. A number of cobalt complexes with class (11) structures are known, the more important mentioned in Table 4. These complexes have either a planar μ-superoxo dioxygen bridge, the compounds thus

being paramagnetic with oxygen-oxygen distances of 1.28 -
1.36 Å; or a non planar μ-peroxo bridge in diamagnetic
species with large variations in the torsional angles
and oxygen-oxygen distances when compared to H_2O_2. The
μ-superoxo complexes can occur in either staggered or
eclipsed conformations.

Class (lll) complexes are postulated to contain
a bent dioxygen-metal bond. This has been observed in
the structure of [Co(bzacen)(O$_2$)]pyridine, bzacen =
$((C_6H_5)C(O^-)CHC(CH_3)N(CH_2^-))_2$ [65] where the cobalt-dioxygen
angle was 126° and the oxygen-oxygen distance 1.26(4) Å.
A number of similar reversible oxygen carrying complexes
have been studied [66-69] and along with oxycoboglobin [70]
and oxyhemoglobin[71,72] have been postulated to contain
similar structures.

A large amount of research has been directed
towards understanding the mode of oxygen addition to
hemoglobin and the matter still requires resolution. The
bonding models of Griffith and Pauling [73] have both been
found to represent structures in synthetic analogues.
The bent dioxygen-metal bond may be the more favoured
current view because of the similarities in the structure
of [Co(bzacen)(O$_2$)] pyridine to that of vitamin B_{12}[74,75]
and hemoglobin[76]. The pyridine geometry is analoguous
to the histidine imidazole ring close to the metal

in the latter two proteins.   Studies on a reversible
iron(II) complex [77] suggest that the oxygenation of
hemoglobin may be heavily influenced by the bulky peptide
chains surrounding the active site.   These may prevent
the formation of a class(ll) bridged complex and ensure
the bent dioxygen bond.

Other dioxygen structures have been postulated
for a variety of synthetic dioxygen complexes [78,79] with
little or no structural justification.

The dioxygen complexes mentioned in this thesis
may be viewed as belonging either purely to class (l)
or as a mixture of class (l) and class (ll) structural
categories.

Table 1

Configurations of Various Dioxygen States

Fig. 1

Dioxygen Molecular Orbital Geometries
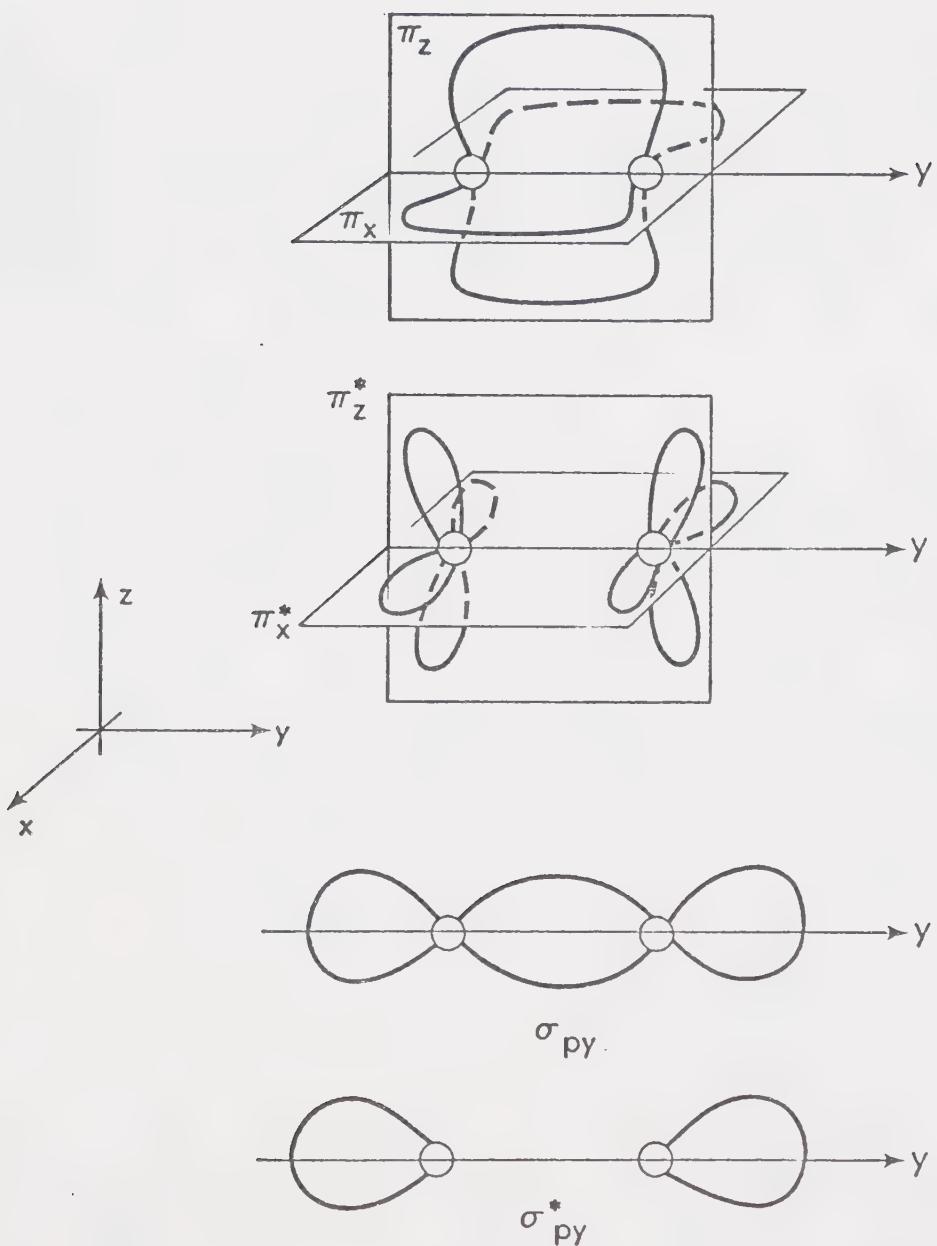
Table 2

A Selection of Simple Oxygen Containing Species

Species	Structure	Oxygen-Oxygen Distance (Å) and Comments	Reference
O_3	O—O—O (bent)	1.278(3)	80
O_2F_2	F—O—O—F, F 87° F	1.217(3) (non planar)	81
O_2^+	linear	1.1227(1)	80
O_2PtF_6	linear	1.17(2)	82
O_2	linear	1.2074(1)	80, 83
KO_2	linear	1.28(2)	80, 84
$B-NaO_2$	linear	1.33(6)	85, 86
$C_6H_5C(O)(O_2)C(O)C_6H_5$	C—O—O—C, C 91° C	1.46(2) (non planar)	87
H_2O_2	H—O—O—H, H 93° H	1.49(1) (non planar)	88
BaO_2	linear	1.49(4)	80, 89
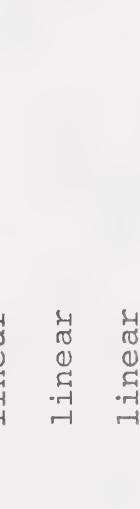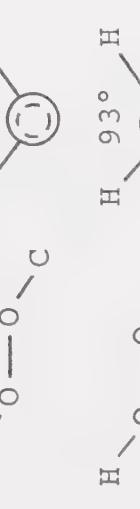
Table 3

A Selection of Class (1) Dioxygen Complexes

Complex	Structure	Oxygen-Oxygen Distance ($\overset{\circ}{A}$)	Reference
$(O_2)IrX(CO)\alpha_2$			
X = Cℓ, α = $P(C_6H_5)_3$	Ir⟨O–O⟩	1.30(3)	17
X = Br, α = $P(C_6H_5)_3$		1.36(4)	90
X = I, α = $P(C_6H_5)_3$		1.47(2), 1.51(2)	18, 10
X = Cℓ, α = $P(C_6H_5)_2(C_2H_5)$		1.46(2)	33
$[(O_2)Ir(2\text{-phos})_2]^+$		1.66(2)	20, 28
$[(O_2)Rh(2\text{-phos})_2]^+$	Rh⟨O–O⟩	1.42(2)	28
$[(O_2)Co(2\text{=phos})_2]^+$	Co⟨O–O⟩	1.42(2)	29
$[(O_2)_4Cr]^{3-}$	Cr⟨O–O⟩	1.41(4)	91
$[(O_2)_3UO]^{4-}$	U⟨O⋯O⟩	1.51(6)	92

Table 4

A Selection of Class (11) Dioxygen Complexes

Complex	Structure	Oxygen-Oxygen Distance (Å) and comments	Reference
$[(NH_3)_5Co(O_2)Co(NH_3)_5]SO_4(HSO_3)_3$	Co—O—O—Co	1.31(3) paramagnetic, planar	93
$[(NH_3)_5Co(O_2)Co(NH_3)_5](NO_3)_5$	..	1.32(2) paramagnetic, planar	94
$[(Cn)_2Co(O_2)(NH_2)Co(Cn)_2](NO_3)_4$		1.36(3) paramagnetic, nearly planar	95
$[(NH_3)_4Co(O_2)(NH_2)Co(NH_3)_4](NO_3)_4$	..	1.32(1) paramagnetic, nearly planar	96
$[(Co(Safen))_2O_2](dmf)_2$		1.34(1) diamagnetic, non planar	97
$[(H_2O)Co(O_2)N_2F_2C_{16}H_{12}O_2-Co(O_2)N_2F_2C_{16}H_{12}]_2$		1.31(3) non planar	98

(Table continued)

Table 4 continued

Complex	Structure	Oxygen–Oxygen Distance (Å) and comments	Reference
$[(NH_3)_5Co(O_2)(NH_3)_5](SO_4)_2$	Co 146° Co	1.47(1) diamagnetic, non planar	99
$[(NH_3)_5Co(O_2)Co(NH_3)_5](SCN)_4$		1.65(3) diamagnetic, planar	100

CHAPTER II

Synthetic Studies

Experimental

  All reactions involving gaseous molecules were performed in sealed vessels. The solutions were degassed by freezing in a liquid nitrogen bath and pumping on the solid material. The gas to be reacted was then introduced and the solution allowed to warm up. This cycle was then repeated several times. Shriver [41] has discussed similar methods for handling air sensitive compounds.

  Infrared spectra were obtained using a Perkin Elmer 421 spectrometer with a standard slit width and the ultraviolet studies were carried out with either a Cary 14 M or a Cary 15 recording spectrophotometer. The former machine was used with a Cary 1411 reflectance attachment and a $MgCO_3$ standard block for the diffuse reflectance spectra. In this study only a white light source was used as the UV lamps did not produce high enough outputs to give a spectrum.

  Melting points were determined on a Koffler Hot Stage and during the slow heating of the sample, the microcrystalline structure was examined continuously by means of a microscope.

The micro- analyses (unless otherwise stated) were performed in this department by Mrs. D. Mahlow and Mrs. A. Dunn. The gas chromatography results were obtained by Mr. A. Clement of this department with a Sargent recorder and using an 8 ft. Linde molecular sieve at 82°C with a helium flow rate of 60 c.c.-min^{-1}. A Cahn Instruments Inc. Gouy Balance was used by Dr. D. Day who undertook the magnetic measurements. All mass spectroscopic studies were performed in this department with either an A.E.I. MS9 high resolution spectrometer or an A.E.I. MS12 medium resolution instrument. Both machines were operated at 70 ev.

Chemicals were either commercially available or prepared as mentioned below.

Methylene Chloride

Three different brands of this solvent were tried with the reactions proceeding only in the brand with the most stringent specifications (Fisher Scientific Co.). This solvent was initially redistilled but as no effect was observed on the reactions when the Fisher samples were used without further treatment, later studies did not include this precaution.

Rhodium Trichloride

This compound was purchased from the Fisher

Scientific Co. or from A.D. Mackay Ltd., the latter material being recrystallized before use.

Tris-triphenylphosphinechlororhodium (I) [RhCℓ(P(C$_6$H$_5$)$_3$)$_3$]

This complex was usually prepared by the method described in the literature [1,3] although one batch was obtained from Fluka AG, Switzerland. The crystals of the orange allotrope of this complex were produced by a variation of the usual method. A solution containing 1 g RhCℓ$_3$·3H$_2$O in 40 ml ethanol was added very slowly to a solution of 10 g triphenylphosphine in 100 ml ethanol, by diffusion through a filter paper over a number of days at 35°C. Microanalytical analysis (Calcd. C, 70.1; H, 4.9; Cℓ, 3.8; P, 10.0; Rh, 11.1; Found: C, 70.0; H, 4.9; Cℓ, 3.8; P, 10.1; Rh, 11.2) were performed by Pascher Microanalytisches Laboratorium, Bonn, Germany. These values were in excellent agreement. The melting point of the compound was 134-136°C.

Crystals of the red form of RhCℓ(P(C$_6$H$_5$)$_3$)$_3$ prepared for the structural study were obtained in an identical manner except that the triphenylphosphine ethanolic solution was added to the rhodium solution. Microanalytical analyses (Found: C, 70.6; H, 4.9) agreed with the literature values although the chlorine analyses proved unsatisfactory, owing to interference

from rhodium or phosphorus. The melting point (138-140°C) agreed with the literature value (138°C). The diffuse reflectance spectra of both forms is given in Fig. 2.

Dioxygen *bis*-triphenylphosphinechlororhodium dimer $[(O_2)RhC\ell(P(C_6H_5)_3)_2\cdot CH_2C\ell_2]_2$

When oxygen was bubbled through a solution containing 0.25 g $RhC\ell(P(C_6H_5)_3)_3$ in 15 ml methylene chloride and the solution slowly evaporated at 7°C for two days a ~50% yield of red-brown diamagnetic crystals was obtained. All measurements were made on this material which appeared to be homogeneous. Carbon and hydrogen analyses (Calcd: C, 57.0; H, 4.1; Found: C, 57.7; H, 4.2) were in reasonable agreement with the for- mulation but the chlorine analysis again proved difficult (Calcd: 13.6; Found: ~15).

Oxygen was positively identified in the gaseous thermal decomposition products by gas chromatography after heating the complex in vacuo to 20°C. The infra- red spectrum of the solid residue showed an absorption (ν, 1120 cm^{-1}) consistent with the formation of complexed triphenylphosphine oxide [43,101]. The dimer undergoes a series of transformations during heating. The first visible transformation (80-85°C) appears to correspond to the complex dissolving in its own solvent of crystal- lisation. This was followed by loss of solvent (110-120°C)

Fig. 2

Reflectance Spectra of $RhCl(P(C_6H_5)_3)_3$
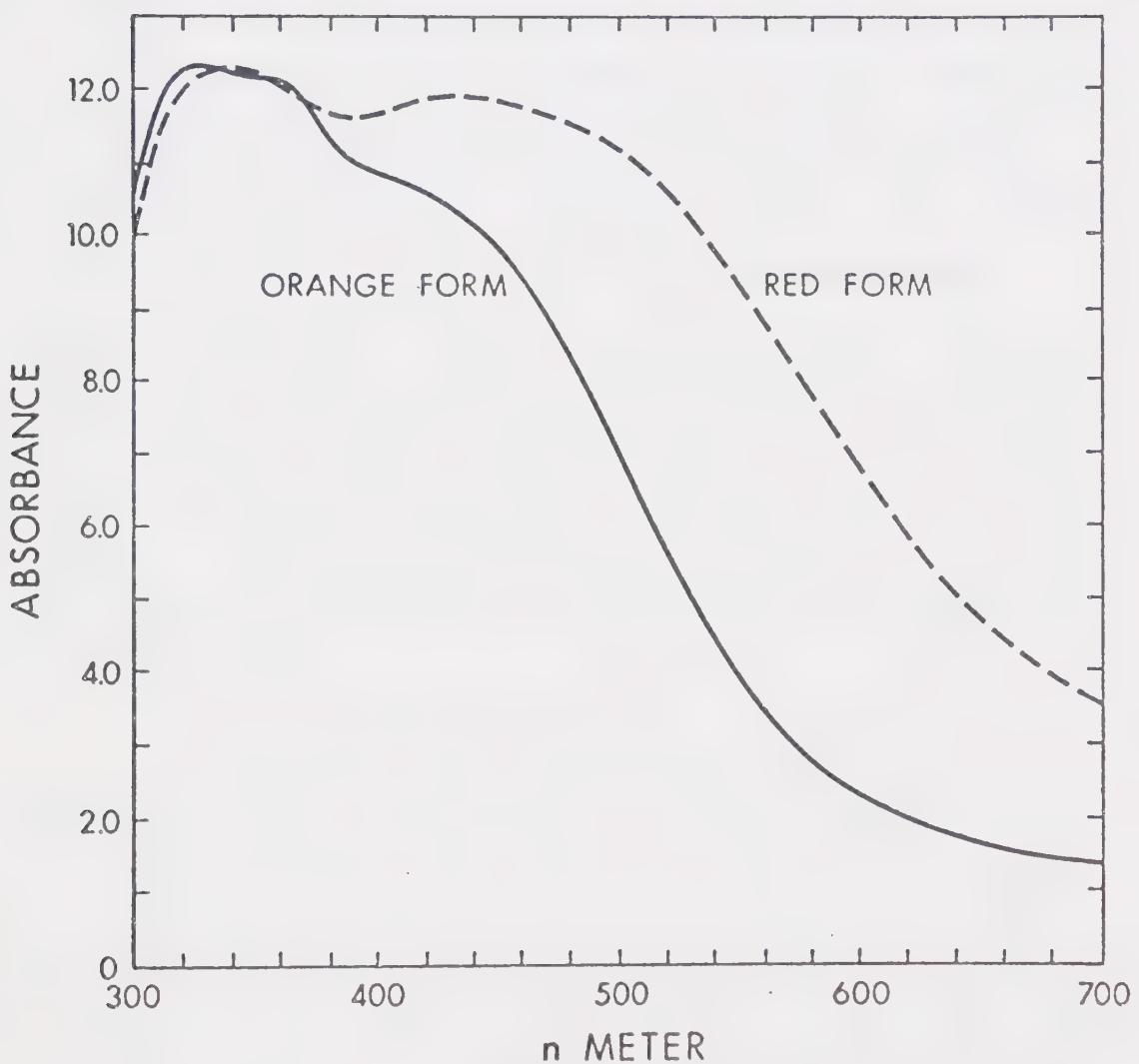
to give a glassy material which when heated to 134°C
tends to explode violently. Thermal gravimetric analyses
(carried out on a DuPont Thermalgravimetric Analyzer)
over two days (Fig. 3) indicated that the complex loses
methylene chloride and a triphenylphosphine below 130°C
(gradual weight loss occurring above this temperature).
At 500°C the mass of the residue corresponded to a mass
of 150 per rhodium atom. Infrared and proton NMR spectra
(Varian A60) verified the presence of free triphenyl-
phosphine in the sublimate collected on the cool sides
of the evacuated reaction tube. Mass spectrometric
studies on the dimer (inlet temperature, 120°C) showed
no parent peak or any recognisable peaks except triphenyl-
phosphine, triphenylphosphine oxide and their degradation
products. Identical behaviour was exhibited by all other
compounds tested although a range of inlet temperatures
was always tried.

$[(O_2)RhC\ell(P(C_6H_5)_3)_2 \cdot CH_2C\ell_2]_2$ is extremely
stable chemically, being inert to either strong acid or
base and almost insoluble in all solvents tested. Re-
crystallisation was thus impossible, however no evidence
of impurities was found. The complex does dissolve after
prolonged exposure to pyridine and an orange crystalline
product is formed. Analysis of this complex proved un-
satisfactory. The infrared spectrum of the dimer (nujol

Fig. 3

$[(O_2)RhC\ell(P(C_6H_5)_3)_2 \cdot CH_2C\ell_2]_2$ Thermal Weight Loss
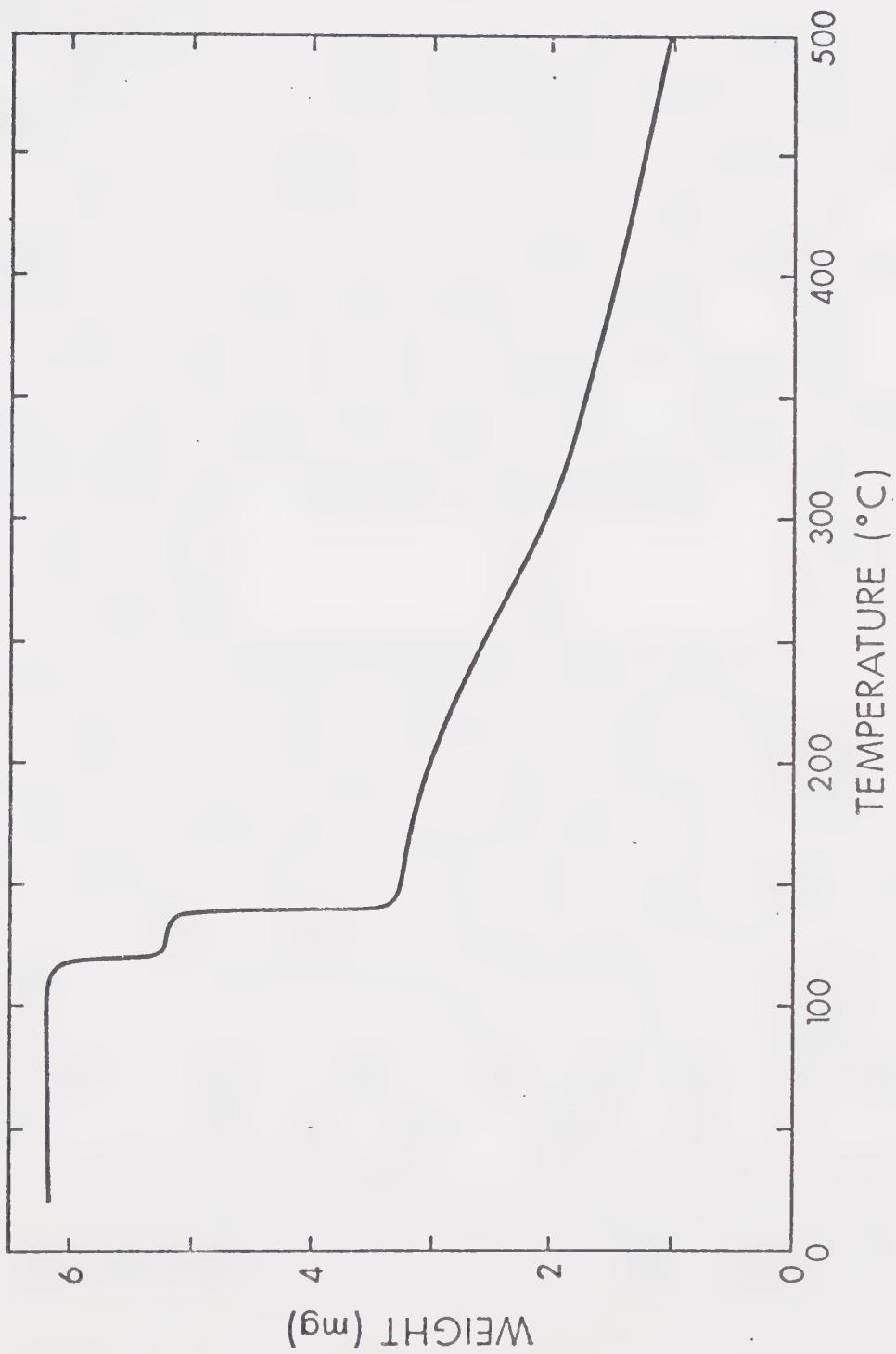
mull, Fig. 4) showed the presence of an absorption at
845 cm^{-1} attributable to rhodium-dioxygen coordination [17].

Dioxygen *tris*-triphenylphosphinechloro rhodium
$[(O_2)RhC\ell(P(C_6H_5)_3)_3 \cdot 2CH_2C\ell_2]$

Oxygen was bubbled through a solution, con-
taining 0.5 g RhCℓ(P(C$_6$H$_5$)$_3$)$_3$ in 15 ml methylene chloride,
for two minutes. After slow evaporation for 2 days at
7°C, yellow crystals of the complex (always accompanied
by the dimer) were filtered off and washed with cyclo-
hexane. The complex may also be produced by adding 0.25 g
triphenylphosphine to 0.25 g RhCℓ(P(C$_6$H$_5$)$_3$)$_3$ and repeating
the above procedure. Handpicked crystals were used in
all subsequent tests.

Microanalytical analyses (Calcd: C, 59.7;
H, 4.4; Found: C, 59.3; H, 4.4) were in reasonable
agreement with the formulation although the chlorine
analysis proved difficult. The compound melted at 82-
84°C and decomposed at 126-128°C. The infrared spectrum
(nujol mull) (Fig. 4) showed an absorption at 880 cm^{-1}
assigned to the coordinated dioxygen. Similar studies
on the products after heating to 200°C in vacuo indicated
the presence of triphenylphosphine oxide in the solid
residue. Oxygen was identified in the gaseous products
by gas chromatography. Confirmation of the solid state
formulation is contained in Chapter IV.   Attempts to

Fig. 4

Infrared Spectra of Dioxygen Derivatives.

ABSORBANCE

$[(O_2)RhCl(P(C_6H_5)_3)_2]_2$

$(O_2)RhCl(P(C_6H_5)_3)_3$

1500   1200   900   600

cm^{-1}
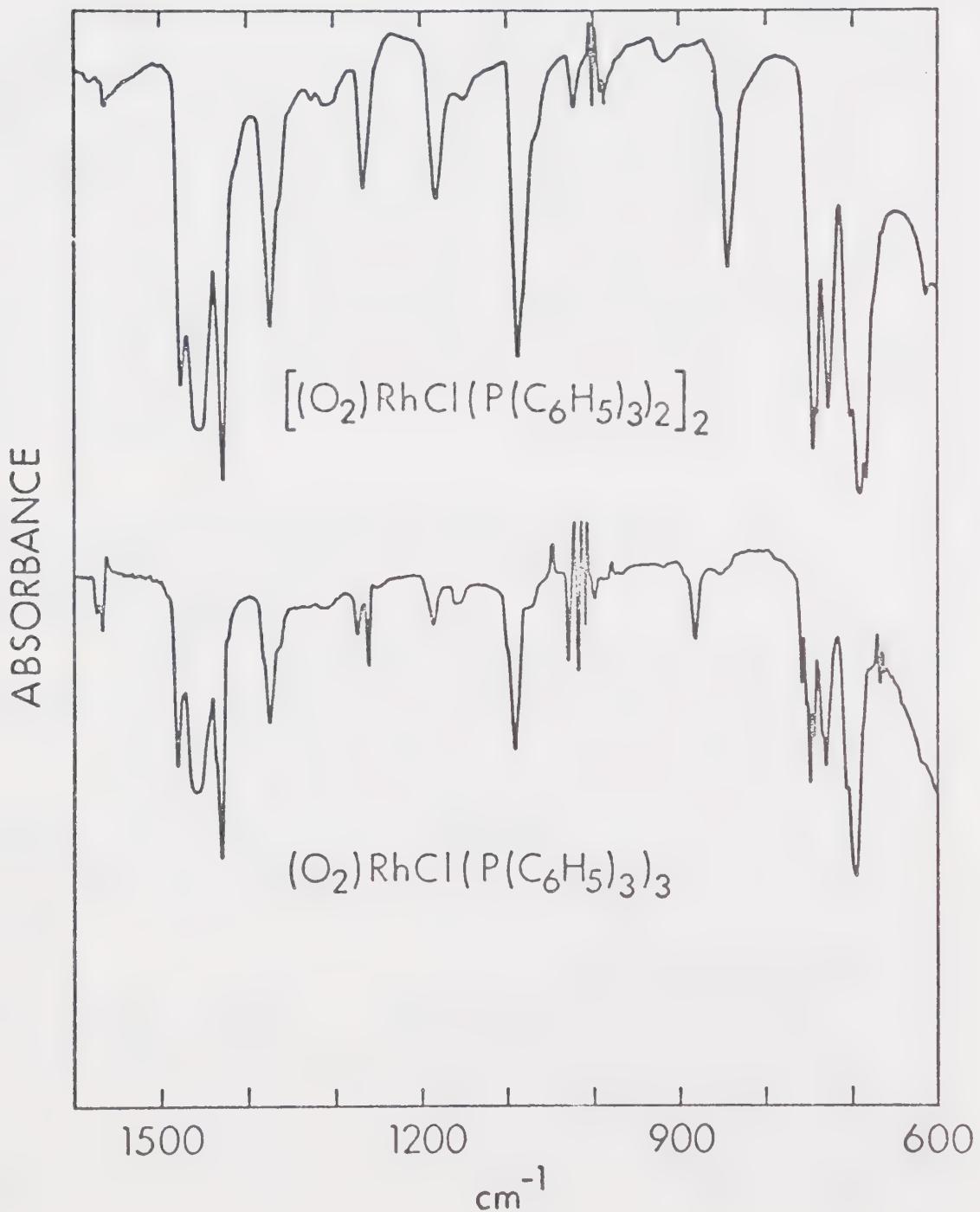
identify the *tris*-phosphine dioxygen complex in solution by the appearance of isosbestic points in the UV spectra were unsuccessful.

Tris-triphenylphosphineiodo rhodium (I) $[RhI(P(C_6H_5)_3)_3]$

   RhI_3 (obtained by treating $RhCl_3$ in a water/ethanol solution with excess lithium iodide) was reacted with triphenylphosphine as described in the literature [3]. Microanalytical analyses (Calcd: C, 63.8; H, 4.4; I, 12.5; Found: C, 63.4; H, 4.6; I, 12.5) were in excellent agreement with the formulation and no evidence of chlorine was found. Melting point, 116-118°C, Lit., 118-120°C.

Dioxygen *bis*-triphenylphosphineiodo rhodium
$[(O_2)RhI(P(C_6H_5)_3)_2]$

   When 3.0 g of $RhI(P(C_6H_5)_3)_3$ in 20 ml methylene chloride was reacted with molecular oxygen for 2 minutes and the solution evaporated at 7°C for two days, black crystals were obtained in about 60% yield. Microanalytical analyses (Calcd: C, 54.9; H, 3.8; I, 16.1; Found: C, 54.2; H, 4.0; I, 16.2) were in good agreement with the formulation. Chlorine analysis failed to indicate the presence of methylene chloride although evidence of methylene chloride was found in the infrared spectrum (nujol mull), $\nu = 740$ cm^{-1}. Strong absorptions

at 857 cm^{-1} with shoulders at 850 cm^{-1} and 838 cm^{-1} were assigned to coordinated dioxygen. Examination of fresh crystals under the microscope showed that a rapid break-down of the crystals was occurring, possibly due to evolution of methylene chloride of crystallisation. This may explain the lack of chlorine in the analysis as this was performed after the infrared spectrum was obtained. The melting point was 166-168°C.

CHAPTER III

The Crystal and Molecular Structures of

$$[(O_2)RhCl(P(C_6H_5)_3)_2 \cdot CH_2Cl_2]_2$$

Experimental

Brown crystals of $[(O_2)RhCl(P(C_6H_5)_3)_2 \cdot CH_2Cl_2]_2$ were obtained using the procedure outlined in Chapter II. These were examined under a microscope and found to be red-yellow pleochroic crystals, a large number of which were twinned. This twinning took the form of a diagonal missetting of the two crystal halves but was avoided by choosing one of a small number of crystals already cleaved in this direction.

Examination of preliminary Weissenberg and precession photographs indicated that the compound crystallized in the triclinic crystal system. The space group was therefore limited to P1 or $P\bar{1}$, the latter being verified by the successful solution and refinement of the structure.

Lattice parameters were found using the technique of centering the reflection in the diffractometer counter windows by adjusting the χ, ω and 2θ circles and checking at -2θ. Crude photographic lattice parameters were then subjected to a least squares refinement [102] to give the best agreement between the calculated and observed 2θ values. Lattice parameters were: a, 13.889(7); b, 13.678(6); c, 11.433(5) Å, α, 105.73(4); β, 115.74(3);

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γ, 100.97(4)°). The density of the compound was measured
by flotation in aqueous potassium iodide as 1.470 g-cm^{-3}
which is in excellent agreement with the calculated den-
sity of 1.469 g-cm^{-3}.

The crystal was mounted on the end of a thin
glass fibre so that the c* axis was coincident with the
φ axis of the diffractometer. Intensity data were collected
on a Picker manual 4-circle diffractometer using the
coupled ω/2θ scan method. Copper K α X-radiation was em-
ployed and the diffractometer settings were calculated
with the programme MIXG2 [103]. Intense peaks were care-
fully scanned to detect any twinning of the crystal and
no evidence (such as splitting) was found. The diffracto-
meter was equipped with a graphite crystal monochromator
(002 reflecting plane) and a 2° take off angle was used.
Each data point was scanned from 2θ - 1° to 2θ + 1° using a
scan speed of 2° per minute. Background counts were
estimated from a linear interpolation of 30 second
stationary counts taken at the limits of the scan.

Data were only measured to 90° in 2θ as indicated
by the preliminary photography. This rapid fall off in
intensity was consistent with a relatively low degree of
order in the crystals. A total of 2151 reflections were
measured and of this number 1658 were found to be statis-
tically reliable using the criterion I ⩽ 3σ. During the
data collection 7 reflections were recollected at intervals

of 8 hours and changes in intensity noted. It was found that the crystal did decompose and that the relationship between the decomposition and time was logarithmic with an additional dependance upon the sin θ/λ value of the reflection. After data collection was completed all peaks with a count rate greater than 10^4 counts-sec^{-1} (i.e., more than the linear counting rate of the counter) were recollected at lower voltages and scaled into the data by comparison with other peaks of lower intensity recollected under the same conditions. The Miller indices of the crystal faces were identified as: 100, $\overline{1}00$, 010, $0\overline{1}0$, 001, $00\overline{1}$, $\overline{3}21$ and the dimensions of the crystal measured to allow an absorption correction to be made.

Reflection data were corrected for Lorentz [104] (L) and polarization (P) effects

$$L = 1 \ /\sin 2\theta$$

$$P = (\cos^2 2\theta_{monochromator} + \cos^2 2\theta) \ /2$$

and the decomposition correction was applied. The absorption correction of the form

$$I = I_o e^{-\mu t}$$

where I_o = uncorrected intensity

μ = linear absorption coeff. (cm^{-1})

t = thickness (cm)

was made using the programme GONO9 [105] with μ = 72.13 cm^{-1}. The transmission factors varied from 0.809 to 0.633. Structure amplitudes ($|F_{rel}|$) and their standard deviations ($\sigma|F_{rel}|$) were then calculated with an uncertainty factor (p) of 0.03 from the equations: [106]

$$|F_{rel}| = \sqrt{I/LP}$$

where $I = [CT - 0.5(t_c/t_b)(B_1 + B_2)]$

now
$$d|F_{rel}| = dI/2\sqrt{LPI}$$

and
$$\frac{d|F_{rel}|}{|F_{rel}|} = \frac{1}{2}\frac{dI}{I}$$

making the approximation that $d|F_{rel}| = \sigma(|F_{rel}|)$ and $dI = \sigma(I)$ then

$$\sigma(|F_{rel}|) = \sigma(I)/2\sqrt{LPI}$$

where
$$\sigma(I) = [CT + 0.25(t_c/t_b)^2(B_1+B_2) + (pI)^2]^{1/2}$$

CT - total integrated peak count obtained in a scan time t_c, B_1 and B_2 being the background counts, each obtained in time t_b.

Solution of Structure and Refinement

The atomic coordinates of the heavy atoms, i.e., rhodium, chlorine and phosphorus were found by calculating a Patterson map [107] using the programme FORDAP [108]. Table 5 contains a listing of the prominent peaks in the Patterson map, together with their assignment and expected magnitude. Approximate coordinates consistent with the space group P$\bar{1}$ were obtained for these atoms.

From the results of the Patterson map it was apparent that the rhodium atoms were located approximately 3.5 Å apart, the molecule thus being dimeric. The other six atoms found were not situated in bridging positions so the molecule appeared to be bridged by either dioxygen or methylene chloride. The rhodium, chlorine and phosphorus atoms were included in the first refinement using SFLS5 [109]. The conventional R factor [110] (R_1) and R_2 (the weighted R factor) were 0.288 and 0.342 respectively, where

$$R_1 = \frac{\Sigma ||F_O| - |F_C||}{\Sigma |F_O|} \text{ and } R_2 = \left[\frac{\Sigma w (|F_O| - |F_C|)^2}{\Sigma w |F_O|^2} \right]^{1/2}$$

and $w = 1/\sigma^2 (F)$

The remaining atoms in the unit cell were located as outlined in Table 6.

The carbon rings of the phenyl groups were constrained to D_{6h} symmetry, with carbon-carbon bond lengths

fixed at 1.392 Å, and refined as rigid bodies to minimize
the number of parameters. The atomic scattering factors
for the rhodium, chlorine, phosphorus and carbon atoms
were derived from Cromer's coefficients [111] and included
the real and imaginary terms for anomalous dispersion [112],
for the rhodium, chlorine and phosphorus atoms. Hydrogen
atoms were included at their calculated positions (carbon-
hydrogen bond lengths, 1.0 Å) with isotropic temperature
factors 10% larger than those of the carbon atoms to which
they were attached. The hydrogen scattering factors were
those of Mason and Robertson [113].

Initially (R_1 = 0.146) (Table 7), the nature of
the methylene chloride electron density peaks indicated
a disordered molecule, however methylene chloride was
included as a single site model and further examination
deferred until later in the refinement. The refinement
(with $\Sigma w (|F_o| - |F_c|)^2$ being minimized) converged to give
a conventional R factor of 0.055 for this model (cycle 10).
At this point an electron density difference map was cal-
culated and residual electron density around the position
of the methylene chloride noted. Several models were
tried to describe this disordered molecule. On the basis
of minimal residual in electron density maps one model
was chosen for the remainder of the refinement. This
model used a single site (single occupancy) for the carbon
atom and one chlorine atom (Cℓ4); the second chlorine atom

being resolved into two sites with variable occupancy factors (Cℓ2, 0.42(4); Cℓ3, 0.62(4)). The single site model for the carbon (C1) and chlorine (Cℓ4) atoms may be physically incorrect but the data do not permit resolution of the separate sites. The total model was then refined to convergence (shift/sigma, ~0.07) to give R_1, 0.044; R_2, 0.055.

Since the observed structure was so novel it was considered necessary to be absolutely certain that the bridging units were dioxygen molecules. When the scattering factors for nitrogen were used for these atoms the atomic thermal parameters assumed physically impossible values and R_1 increased to 0.051. Thus all evidence, both chemical (Chapter 2) and crystallographic (a Hamilton test [114] rejects the N_2 at better than the 0.005 confidence level) confirms the assignment of oxygen for these atoms.

A final electron density difference map was then calculated. The largest positive and negative peaks were 0.4 and -0.4 e-$\overset{\circ}{A}^{-3}$ respectively (c.f. carbon ~3 e-$\overset{\circ}{A}^{-3}$) and were located in the vicinity of the disordered methylene chloride molecule.

The atomic coordinates and their standard deviations of all atoms were then used to calculate inter-atomic bond lengths, angles and intra and intermolecular nonbonded contacts with their respective standard deviations, with the programme ORFFE II [115].

As the equivalent isotropic temperature factor
of the chlorine atom (Cℓ1) was relatively large (4.17)
a riding correction was applied to the rhodium-chlorine
bond length. This compensates for the false shortening
of this bond caused by the thermal motion description and
its interpretation by the bond length programme. A similar
correction was also applied to the rhodium-phosphorus
bond lengths as a check. The thermal motion in these
latter atoms was small so only slight changes were expected.
This was indeed found to be the case. All atoms in these
corrections were assumed to ride on a "stationary"
rhodium atom.

Table 5

Assignment of Patterson Map Peaks

Peak Coordinates*			Relative Height (origin=999)	Assignment	Calculated Height	Calculated Coordinates (from Solution)		
u	v	w				u'	v'	w'
0.172,	-0.126,	0.124	228	$2x_a, 2y_a, 2z_a$	320	0.156,	-0.114,	0.132
-0.185,	0.116,	-0.136	236	$2\bar{x}_a, 2\bar{y}_a, 2\bar{z}_a$	320	-0.156,	0.114,	-0.132
-0.080,	-0.060,	-0.214	102	$x_a-x_b, y_a-y_b, z_a-z_b$	120	-0.083,	-0.060,	-0.250
-0.269,	0.050,	-0.370	108	$\bar{x}_a-x_b, \bar{y}_a-y_b, \bar{z}_a-z_b$	120	-0.273,	0.053,	-0.383
0.004,	0.160,	-0.006	158	$x_a-x_c, y_a-y_c, z_a-z_c$	107	0.032,	0.178,	0.022
-0.164,	0.292,	-0.110	123	$\bar{x}_a-x_c, \bar{y}_a-y_c, \bar{z}_a-z_c$	107	-0.162,	0.292,	-0.110
-0.164,	-0.038,	-0.006	106	$x_a-x_d, y_a-y_d, z_a-z_d$	107	-0.170,	-0.044,	-0.007
-0.353,	0.072,	-0.136	112	$x_a-x_d, y_a-y_d, z_a-z_d$	107	-0.360,	0.070,	-0.139

Space group P$\bar{1}$ solution a = Rh x, 0.078; $\bar{y}$, 0.060; z, 0.065

b = Cℓl x, 0.175, 0.005, 0.292

c = Pl x, 0.080, -0.226, 0.058

d = P2 x, 0.259, -0.009, 0.072

* These peaks with their combinations were the fourteen strongest peaks observed.

Table 6

Structure Solution Refinement Sequence

Refinement Cycle	Atoms used in Phasing	R_1	Atoms Located in Diff. Map.
1	Rh, Cℓ1, P1, P2,	0.288	O1, O2, C111–C116, C131–C136, C222–C226
2	Rh, Cℓ1, P1, P2, O1, O2 C111–C116, C131–C136, C222–C226	0.204	
3	∴	0.186	C121–C126, C211–C216, C231–C236
4	Rh, Cℓ1, P1, P2, O1, O2 C111–C116, C121–C126, C131–C136, C211–C216, C221–C226, C231–C236	0.146	Methylene chloride located (included as a single site model)

Table 7

Refinement Sequence for Model

Refinement Cycle	Model Description	R_1	R_2
5	All atoms included, anomalous dispersion correction applied	0.112	0.136
6	..	0.091	0.116
7	Central atoms assigned anisotropic thermal parameters	0.077	0.090
8	..	0.071	0.083
9	Hydrogen atoms included	0.061	0.073
10	..	0.055	0.066
11	Methylene chloride represented as disordered model	0.049	0.060
12	..	0.046	0.057
13	..	0.044	0.055
14	Oxygen atoms replaced by nitrogen atoms	0.053	0.071
15	..	0.051	0.069

Results

Table 8 gives the observed ($|F_o|$) and calculated ($|F_c|$) structure amplitudes (electrons x 10). The atomic coordinates of all atoms are listed in Table 9 and the anisotropic temperature factors (U_{ij}) for the central atoms are given in Table 10. Interatomic distances (Table 11), interatomic angles (Table 12), intramolecular and intermolecular non bonded-contacts (Tables 13 and 14 respectively) are included with the standard deviations in parentheses.

A view [116] of the whole molecule is shown in Fig. 5. The central coordination geometry is represented in Fig. 6 and a view down the Pl-O2' axis is given in Fig. 7.

Table 8

Observed and Calculated Structure Amplitudes (electrons x 10)

H	K	FOBS	FCAL
L = 0			
1	0	1400	1438
2	0	288	278
3	0	986	916
4	0	749	755
5	0	1232	1186
6	0	727	687
7	0	267	245
-10	1	390	395
-9	1	306	326
-8	1	292	200
-6	1	370	378
-5	1	594	629
-4	1	859	835
-3	1	461	473
-2	1	341	324
-1	1	181	79
0	1	1573	1588
1	1	510	492
2	1	722	735
3	1	357	353
4	1	172	170
6	1	481	480
7	1	410	402
8	1	117	134
-10	2	266	285
-9	2	324	331
-8	2	283	291
-7	2	577	522
-5	2	110	105
-4	2	531	501
-3	2	137	62
-2	2	467	529
-1	2	371	378
0	2	253	257
1	2	927	937
2	2	749	759
3	2	579	611
4	2	165	148
6	2	141	159
7	2	182	207
-10	3	218	220
-9	3	247	248
-8	3	410	373
-7	3	489	453
-6	3	186	165
-4	3	111	83
-3	3	1307	1313
-2	3	1325	1256
-1	3	260	265
0	3	1710	1740
1	3	1326	1362
2	3	463	474
3	3	230	225
4	3	107	105
6	3	571	610
7	3	450	401
8	3	188	144
-8	4	386	426
-7	4	595	615
-6	4	134	146
-5	4	216	192
-4	4	696	684
-3	4	1122	1088
-2	4	792	790
-1	4	418	397
0	4	713	730
1	4	1049	1053
2	4	161	157
4	4	475	480
6	4	463	411
7	4	323	295
-10	5	176	187
-8	5	276	306
-7	5	591	573
-6	5	559	507
-4	5	386	392
-3	5	756	734
-2	5	870	845
-1	5	1035	1023
0	5	186	187
1	5	488	482
2	5	185	165
3	5	223	195
4	5	449	441
5	5	397	37C
-8	6	412	405
-7	6	708	683
-6	6	36C	345
-5	6	143	155
-3	6	715	722
-2	6	794	820
-1	6	1159	1155
0	6	333	323
2	6	264	269
3	6	417	420
4	6	694	688
5	6	568	509
-9	7	289	280
-8	7	315	289
-7	7	798	791
-6	7	658	636
-5	7	650	638
-3	7	506	480
-2	7	874	869
-1	7	696	719
0	7	203	226
2	7	138	132
4	7	390	374
5	7	324	327
-9	8	493	464
-7	8	555	565
-6	8	644	630
-5	8	470	462
-4	8	294	314
-2	8	374	362
-1	8	133	111
0	8	198	190
2	8	202	143
4	8	279	276
-8	9	171	137
-7	9	234	241
-6	9	360	343
-5	9	266	250
-4	9	365	335
-2	9	224	252
-1	9	197	174
0	9	160	155
2	9	136	120
-7	10	221	213
-6	10	331	323
-5	10	144	144
-4	10	380	356
-3	10	170	195
-2	10	229	222
-1	10	313	292
0	10	242	235
L = 1			
2	-11	259	261
4	-11	589	576
4	-11	471	467
5	-11	235	261
0	-10	137	86
3	-10	272	298
4	-10	330	347
6	-10	262	260
0	-9	400	401
3	-9	478	501
4	-9	515	528
7	-9	198	195
-4	-8	205	211
0	-8	442	446
1	-8	576	574
2	-8	272	243
3	-8	389	401
4	-8	595	619
5	-8	477	482
6	-8	365	330
7	-8	224	167
8	-8	225	188
-5	-7	214	225
-4	-7	335	341
-2	-7	546	582
-1	-7	172	178
0	-7	208	192
1	-7	698	708
2	-7	391	393
3	-7	128	109
4	-7	341	355
5	-7	493	492
6	-7	514	539
7	-7	333	338
9	-7	169	140
-6	-6	253	260
-5	-6	519	550
-4	-6	448	468
-3	-6	147	128
-2	-6	293	320
-1	-6	153	204
0	-6	916	923
1	-6	1308	1320
2	-6	818	826
4	-6	285	273
5	-6	242	270
6	-6	391	448
7	-6	399	418
8	-6	320	291
-5	-5	536	538
-4	-5	595	611
-3	5	498	485
-1	-5	319	341
0	-5	445	429
1	-5	1247	1257
2	-5	1276	1257
3	-5	525	531
4	-5	175	180
7	-5	528	515
8	-5	351	341
-8	-4	212	223
-7	-4	345	360
-6	-4	603	644
-4	-4	725	721
-3	-4	355	377
-2	-4	125	107
-1	-4	290	309
1	-4	828	819
3	-4	243	221
4	-4	450	431
5	-4	395	397
6	-4	196	165
7	-4	184	212
8	-4	312	300
9	-4	173	195
-9	-3	206	232
-7	-3	173	148
-6	-3	411	400
-5	-3	343	322
-4	-3	188	194
-2	-3	221	217
-1	-3	1012	994
0	-3	633	639
1	-3	534	491
2	-3	1181	1141
4	-3	182	175
5	-3	325	330
6	-3	135	171
7	-3	605	657
8	-3	375	405
9	-3	193	182
-7	-2	280	289
-6	-2	404	370
-4	-2	384	415
-3	-2	1061	1095
-2	-2	281	264
-1	-2	612	651
0	-2	445	405
2	-2	1421	1401
3	-2	188	180
4	-2	391	382
5	-2	343	344
7	-2	471	526
8	-2	505	547
9	-2	393	390
-8	-1	142	131
-7	-1	377	356
-6	-1	364	413
-5	-1	516	537
-3	-1	1526	1511
-2	-1	967	960
-1	-1	1021	943
0	-1	1026	1071
1	-1	424	461
2	-1	418	405
3	-1	590	610
4	-1	266	265
5	-1	492	517
6	-1	578	605
8	-1	428	406
9	-1	366	399
-7	0	469	489
-6	0	7C5	720
-5	0	700	678
-4	0	433	458
-3	0	725	668
-2	0	361	275
-1	0	1666	1707
0	0	1463	1476
1	0	508	524
2	0	667	629
4	0	777	741
5	0	946	974
6	0	806	796
8	0	157	170
9	0	149	140
-10	1	224	199
-9	1	315	306
-8	1	318	285
-7	1	235	247
-6	1	956	957
-5	1	901	907
-4	1	427	421
-3	1	142	105
-2	1	95	70
-1	1	725	727
0	1	1036	1066
1	1	684	677
3	1	289	297
4	1	123	121
5	1	568	569
6	1	816	793
7	1	249	208
-10	2	288	275
-8	2	502	535
-7	2	188	253
-6	2	341	335
-5	2	640	637
-4	2	533	558
-3	2	774	715
-1	2	142	125
0	2	960	907
1	2	403	412
2	2	246	249
3	2	261	265
5	2	584	550
6	2	535	516
7	2	166	177
-10	3	299	158
-8	3	592	602
-7	3	183	171
-6	3	364	374
-5	3	603	611
-4	3	691	675
-3	3	279	265
-2	3	794	779
-1	3	172	201
0	3	628	632
1	3	370	366
2	3	189	190
3	3	145	148
4	3	156	179
5	3	511	508
6	3	609	619
7	3	469	476
-10	4	152	158
-9	4	237	214
-8	4	507	500
-7	4	398	345
-6	4	328	337
-5	4	351	350
-4	4	483	483
-3	4	825	831
-2	4	661	653
-1	4	154	139
0	4	352	328
1	4	353	356
2	4	214	236
3	4	576	561
4	4	252	265
5	4	297	308
6	4	490	479
-9	5	208	155
-8	5	554	547
-7	5	712	703
-6	5	215	166
-5	5	366	382
-4	5	612	589
-3	5	972	966
-2	5	705	692
-1	5	380	340
0	5	150	119
2	5	714	705
3	5	710	711
4	5	447	418
6	5	235	204
-8	6	696	705
-7	6	730	768
-5	6	265	242
-4	6	425	408
-3	6	352	363
-2	6	580	570
-1	6	721	703
2	6	370	362
3	6	561	582
4	6	727	709
5	6	223	248
-10	7	147	126
-8	7	668	621
-7	7	703	702
-6	7	498	491
-5	7	214	185
-3	7	360	369
-2	7	503	494
-1	7	483	471
0	7	265	262
1	7	158	205
3	7	497	507
4	7	532	551
-9	8	199	196
-8	8	418	381
-7	8	825	785
-6	8	443	415
-5	8	234	240
-4	8	249	252
-2	8	159	173
-1	8	381	373
0	8	374	384
1	8	181	201
-7	9	504	487
-4	9	227	226
-3	9	135	110
-2	9	316	307
-1	9	218	222
-7	10	366	377
-4	10	248	265
-2	10	171	210
-1	10	222	204
L = 2			
1	-11	145	162
2	-11	500	521
3	-11	608	614
4	-11	170	144
-2	-10	374	335
-1	-10	241	224
0	-10	147	160
2	-10	223	257
3	-10	591	609
-4	-9	310	341
-3	-9	156	124
-2	-9	334	342
-1	-9	536	563
0	-9	357	363
1	-9	248	226
2	-9	368	354
3	-9	687	666
5	-9	155	124
-5	-8	216	277
-4	-8	280	297
-3	-8	166	169
-2	-8	234	259

Table 8 (continued)

H	K	FOBS	FCAL
L = 2**			
-1	-8	436	432
0	-8	224	244
1	-8	393	393
2	-8	336	331
3	-8	528	553
4	-8	265	267
6	-8	197	195
8	-8	410	396
-5	-7	288	277
-4	-7	433	442
-3	-7	205	198
-2	-7	539	549
-1	-7	496	544
0	-7	836	866
1	-7	664	693
3	-7	786	773
4	-7	518	539
5	-7	460	442
6	-7	266	273
7	-7	420	369
-7	-6	289	290
-6	-6	250	237
-5	-6	538	531
-4	-6	721	751
-3	-6	206	220
-2	-6	737	742
0	-6	1203	1245
1	-6	897	904
2	-6	481	472
3	-6	305	292
4	-6	275	281
5	-6	513	459
6	-6	516	525
7	-6	654	647
8	-6	215	213
-7	-5	147	169
-6	-5	209	215
-5	-5	701	749
-4	-5	1062	1035
-3	-5	427	456
-2	-5	204	196
-1	-5	581	594
0	-5	741	738
1	-5	854	860
2	-5	292	276
3	-5	240	220
4	-5	172	168
5	-5	236	220
6	-5	511	531
7	-5	508	555
8	-5	180	203
-8	-4	207	208
-7	-4	601	586
-6	-4	220	210
-5	-4	130	130
-4	-4	365	376
-3	-4	599	628
-2	-4	872	871
-1	-4	374	343
0	-4	518	526
1	-4	183	208
2	-4	369	366
3	-4	542	507
4	-4	178	181
5	-4	240	211
6	-4	266	284
7	-4	462	466
-8	-3	183	176
-7	-3	330	340
-6	-3	409	400
-4	-3	912	929
-3	-3	563	543
-2	-3	328	338
-1	-3	260	275
1	-3	481	478
2	-3	1117	1128
3	-3	203	223
6	-3	408	402
7	-3	730	725
8	-3	347	356
-8	-2	266	305
-7	-2	674	688
-6	-2	388	386
-5	-2	386	385
-4	-2	1425	1427
-3	-2	788	772
-2	-2	1241	1174
0	-2	748	738
1	-2	1485	1457
2	-2	306	295
3	-2	237	225
4	-2	217	236
5	-2	315	326
6	-2	188	146
7	-2	552	590
8	-2	527	566
-8	-1	338	334
-7	-1	453	470
-6	-1	350	339
-5	-1	361	357
-4	-1	425	425
-3	-1	1235	1196
-1	-1	801	794
0	-1	535	548
1	-1	499	506
3	-1	684	695
4	-1	556	597
5	-1	683	704
6	-1	305	305
7	-1	338	351
8	-1	448	452
-8	0	331	311
-7	0	747	715
-6	0	1268	1245
-4	0	605	611
-3	0	1257	1327
-2	0	231	213
-1	0	1584	1652
0	0	222	245
1	0	195	186
2	0	429	397
3	0	661	667
4	0	799	761
5	0	679	653
6	0	486	480
8	0	312	288
-11	1	427	445
-10	1	227	241
-8	1	126	120
-7	1	976	988
-6	1	1054	1066
-5	1	130	134
-4	1	317	270
-3	1	676	626
-2	1	1578	1532
-1	1	1121	1080
0	1	132	85
1	1	111	81
2	1	131	138
3	1	453	435
4	1	510	537
5	1	660	677
6	1	385	386
-11	2	436	443
-10	2	437	413
-9	2	305	290
-8	2	473	421
-7	2	624	647
-6	2	914	922
-5	2	781	784
-3	2	356	357
-2	2	553	580
-1	2	165	173
0	2	351	355
1	2	434	444
2	2	160	162
3	2	299	269
4	2	520	526
5	2	606	587
6	2	231	224
-11	3	391	371
-10	3	286	294
-9	3	239	217
-8	3	435	430
-7	3	263	243
-6	3	859	817
-5	3	511	502
-4	3	502	531
-3	3	410	400
-2	3	742	728
0	3	343	338
1	3	473	488
3	3	262	251
4	3	355	316
5	3	412	388
6	3	484	469
-10	4	194	213
-9	4	193	227
-8	4	164	175
-7	4	219	198
-6	4	545	527
-5	4	338	334
-4	4	263	274
-3	4	157	181
-1	4	234	258
0	4	520	545
1	4	473	459
2	4	293	280
4	4	288	267
5	4	463	451
6	4	331	337
-10	5	292	308
-9	5	458	467
-8	5	526	541
-7	5	221	168
-6	5	627	628
-5	5	487	496
-4	5	640	640
-3	5	205	247
-2	5	559	569
0	5	281	264
1	5	416	432
2	5	712	730
3	5	484	510
4	5	135	150
-10	6	336	354
-9	6	541	505
-8	6	857	812
-7	6	168	144
-6	6	180	193
-4	6	178	170
-3	6	683	670
-2	6	1091	1092
-1	6	476	472
1	6	489	488
2	6	616	623
3	6	735	717
4	6	336	309
-10	7	256	226
-9	7	417	391
-8	7	772	751
-7	7	515	515
-6	7	237	249
-5	7	131	109
-3	7	141	121
-2	7	628	652
-1	7	501	457
1	7	185	198
2	7	235	221
3	7	483	502
-8	8	390	391
-7	8	494	462
-6	8	248	240
-5	8	248	227
-4	8	283	263
-2	8	457	477
-1	8	295	285
-8	9	222	232
-7	9	222	190
-6	9	212	211
-2	9	286	265
-1	9	335	341
-4	10	206	229
L = 3**			
0	-11	239	229
1	-11	363	350
2	-11	447	472
3	-11	352	344
-3	-10	294	265
2	-10	235	254
3	-10	352	352
-3	-9	347	324
-2	-9	383	377
-1	-9	207	187
1	-9	220	202
2	-9	190	222
3	-9	210	209
4	-9	148	124
7	-9	193	215
-6	-8	304	302
-5	-8	225	204
-3	-8	447	459
-2	-8	635	638
-1	-8	416	409
2	-8	399	391
3	-8	402	424
4	-8	230	229
5	-8	199	201
7	-8	172	173
-7	-7	229	199
-6	-7	149	150
-5	-7	365	378
-3	-7	490	511
-2	-7	660	661
-1	-7	594	602
0	-7	466	459
1	-7	158	170
2	-7	503	451
3	-7	526	516
4	-7	547	551
5	-7	522	541
6	-7	375	402
-8	-6	165	183
-6	-6	462	459
-5	-6	629	633
-3	-6	409	400
-2	-6	295	291
-1	-6	510	516
0	-6	433	434
1	-6	797	761
2	-6	635	601
4	-6	800	817
5	-6	528	570
6	-6	757	776
7	-6	478	456
-6	-5	581	551
-5	-5	950	915
-4	-5	597	606
-2	-5	468	477
-1	-5	516	535
0	-5	729	713
1	-5	519	537
2	-5	579	592
3	-5	387	405
5	-5	482	496
7	-5	306	281
-9	-4	298	342
-8	-4	273	276
-6	-4	206	217
-5	-4	823	843
-4	-4	496	475
-3	-4	277	280
-2	-4	129	161
-1	-4	353	345
0	-4	114	136
1	-4	297	280
2	-4	256	263
3	-4	286	295
5	-4	613	562
6	-4	411	436
8	-4	183	143
-9	-3	189	154
-8	-3	311	360
-7	-3	449	463
-5	-3	370	379
-4	-3	400	399
-3	-3	128	117
-2	-3	629	664
-1	-3	558	550
0	-3	837	834
1	-3	768	760
2	-3	493	471
3	-3	288	317
5	-3	241	270
6	-3	602	649
7	-3	505	534
-9	-2	169	159
-8	-2	305	270
-7	-2	434	394
-5	-2	384	377
-4	-2	1297	1314
-3	-2	174	128
-2	-2	827	822
-1	-2	243	222
0	-2	300	297
1	-2	646	635
2	-2	574	583
3	-2	734	760
4	-2	252	261
5	-2	248	262
6	-2	425	475
7	-2	591	620
-10	-1	170	175
-9	-1	296	275
-8	-1	446	432
-7	-1	458	469
-6	-1	273	264
-5	-1	645	632
-4	-1	1325	1345
-2	-1	625	603
-1	-1	652	637
1	-1	448	456
2	-1	932	982
3	-1	973	972
4	-1	506	535
6	-1	209	203
7	-1	532	512
-11	0	229	235
-9	0	315	332
-8	0	450	497
-7	0	655	681
-6	0	511	485
-4	0	508	458
-3	0	308	316
-2	0	554	545
-1	0	892	860
0	0	623	609
1	0	190	196
2	0	307	296
3	0	971	977
4	0	710	727
5	0	623	621
7	0	188	229
-11	1	425	361
-9	1	245	239
-8	1	457	449
-7	1	866	862
-6	1	799	777
-5	1	252	269
-4	1	434	424
-3	1	205	213
-1	1	805	824
0	1	1052	1047
2	1	448	449
3	1	739	714
4	1	520	509
5	1	410	404
-11	2	562	509
-10	2	242	248
-9	2	211	238
-8	2	270	267
-7	2	757	754
-6	2	779	778
-5	2	741	685
-4	2	336	338
-3	2	333	327
-2	2	869	871
-1	2	753	745
0	2	509	504
2	2	272	269
3	2	358	336
4	2	548	543
5	2	145	126
6	2	151	151
-11	3	437	424
-10	3	199	195
-7	3	118	134
-6	3	346	356
-5	3	289	284

Table 8 (continued)

Column group 1

H	K	FOBS	FCAL
L = 3**			
-4	3	157	128
-3	3	741	783
-2	3	172	153
-1	3	170	153
0	3	534	528
1	3	277	296
2	3	167	152
3	3	125	113
4	3	433	426
5	3	329	336
-9	4	175	155
-8	4	199	169
-7	4	161	136
-6	4	359	351
-4	4	189	206
-3	4	272	282
-2	4	302	304
-1	4	586	590
0	4	758	788
1	4	305	285
2	4	146	126
4	4	254	248
-11	5	399	377
-10	5	311	297
-9	5	309	296
-8	5	207	184
-7	5	143	105
-6	5	239	225
-5	5	839	832
-4	5	737	698
-3	5	340	354
-1	5	601	602
0	5	874	889
1	5	583	549
2	5	405	430
3	5	165	125
-10	6	491	496
-9	6	703	728
-8	6	492	509
-7	6	180	206
-5	6	479	482
-4	6	738	788
-3	6	721	730
-2	6	630	611
0	6	484	492
1	6	417	428
2	6	545	579
-9	7	463	453
-8	7	636	613
-7	7	586	572
-6	7	311	281
-5	7	270	273
-4	7	272	245
-3	7	665	657
-2	7	642	665
-8	8	288	304
-7	8	293	288
-6	8	234	219
-5	8	191	184
-3	8	479	495
-2	8	387	352
0	8	157	105
-7	9	305	335
-4	9	221	252
-3	9	496	479
L = 4**			
0	-11	237	228
1	-11	182	200
2	-11	385	376
3	-11	177	170
-3	-10	411	396
-2	-10	191	204
2	-10	277	264
-4	-9	347	333
-3	-9	336	359
-2	-9	175	161
2	-9	203	230
3	-9	298	275
4	-9	149	168
6	-9	245	214
-5	-8	211	194
-4	-8	451	453
-3	-8	510	514

Column group 2

H	K	FOBS	FCAL
-2	-8	370	362
0	-8	180	191
2	-8	288	291
3	-8	388	385
4	-8	490	488
5	-8	233	216
-7	-7	241	211
-6	-7	312	287
-5	-7	215	194
-4	-7	409	407
-3	-7	578	581
-2	-7	449	472
-1	-7	460	442
0	-7	284	285
2	-7	710	703
3	-7	391	428
4	-7	741	717
5	-7	269	246
6	-7	185	155
7	-7	408	415
-8	-6	452	384
-7	-6	375	362
-6	-6	477	482
-4	-6	176	202
-3	-6	355	376
-2	-6	491	480
-1	-6	502	523
0	-6	382	391
1	-6	554	535
2	-6	131	119
3	-6	728	745
4	-6	753	730
5	-6	693	694
6	-6	550	573
-9	-5	201	186
-8	-5	228	195
-7	-5	269	267
-6	-5	636	656
-5	-5	809	801
-3	-5	135	110
-2	-5	251	241
-1	-5	332	337
0	-5	782	757
1	-5	964	914
3	-5	597	602
4	-5	313	281
5	-5	583	640
6	-5	454	498
-9	-4	178	212
-7	-4	267	278
-6	-4	439	452
-5	-4	665	660
-4	-4	128	138
-3	-4	524	538
-2	-4	190	209
0	-4	129	111
1	-4	470	506
4	-4	301	313
5	-4	187	216
6	-4	208	217
-10	-3	443	426
-9	-3	367	360
-7	-3	193	191
-6	-3	270	235
-5	-3	593	590
-4	-3	401	379
-3	-3	266	245
-2	-3	152	167
-1	-3	151	160
0	-3	427	425
1	-3	494	512
4	-3	271	295
5	-3	383	365
6	-3	428	456
-10	-2	192	172
-9	-2	215	204
-8	-2	285	319
-7	-2	177	183
-5	-2	736	738
-3	-2	215	227
-2	-2	582	575
0	-2	1181	1151
1	-2	989	1000
2	-2	671	688

Column group 3

H	K	FOBS	FCAL
4	-2	172	187
5	-2	326	307
6	-2	484	513
-11	-1	203	248
-10	-1	212	227
-9	-1	402	332
-8	-1	251	200
-5	-1	210	198
-4	-1	251	278
-3	-1	797	779
-2	-1	942	920
-1	-1	612	614
0	-1	617	611
1	-1	1052	1040
2	-1	999	1001
3	-1	553	566
4	-1	286	289
5	-1	135	114
6	-1	396	414
-10	0	567	562
-9	0	751	717
-8	0	417	407
-7	0	583	567
-6	0	229	232
-5	0	293	312
-4	0	810	822
-3	0	756	719
-2	0	801	793
-1	0	721	736
0	0	471	448
1	0	425	440
2	0	634	661
3	0	545	532
4	0	380	371
5	0	245	256
-10	1	257	276
-9	1	368	388
-8	1	682	699
-7	1	655	671
-6	1	369	352
-5	1	206	185
-2	1	1030	1017
-1	1	844	845
0	1	120	67
1	1	659	660
2	1	484	488
3	1	176	216
4	1	244	238
-11	2	278	236
-8	2	155	147
-6	2	760	752
-5	2	747	756
-4	2	515	482
-2	2	800	802
-1	2	699	712
0	2	196	167
1	2	446	427
2	2	170	192
4	2	192	206
-11	3	284	268
-8	3	136	86
-7	3	348	343
-6	3	436	444
-4	3	317	313
-3	3	117	139
-2	3	514	527
-1	3	637	658
0	3	276	266
2	3	147	132
4	3	238	194
-9	4	190	189
-7	4	162	181
-5	4	363	354
-4	4	266	254
-2	4	754	710
-1	4	905	907
0	4	306	312
1	4	146	150
-11	5	247	243
-10	5	200	232
-9	5	289	263
-8	5	275	285
-7	5	150	155
-6	5	331	357

Column group 4

H	K	FOBS	FCAL
-5	5	562	547
-4	5	291	260
-3	5	434	432
-1	5	767	794
0	5	561	535
2	5	336	325
-10	6	443	438
-9	6	761	701
-8	6	514	469
-7	6	414	396
-6	6	769	781
-5	6	729	738
-4	6	486	468
-3	6	502	484
-1	6	348	366
0	6	192	178
1	6	428	441
-9	7	500	513
-8	7	338	360
-7	7	362	380
-5	7	498	475
-4	7	531	541
-3	7	174	190
0	7	426	418
-8	8	223	239
-4	8	507	501
L = 5**			
-3	-10	305	316
-1	-10	145	117
0	-10	149	120
1	-10	346	338
2	-10	511	502
-4	-9	272	278
-3	-9	189	177
-1	-9	146	152
0	-9	230	227
1	-9	169	182
2	-9	240	262
3	-9	262	259
-4	-8	371	394
-3	-8	288	290
-2	-8	236	226
-1	-8	144	113
1	-8	400	397
2	-8	711	702
3	-8	617	554
5	-8	288	274
-5	-7	308	303
-4	-7	521	504
-3	-7	338	331
-2	-7	305	323
-1	-7	392	401
0	-7	230	210
1	-7	705	680
2	-7	831	843
3	-7	783	769
4	-7	287	286
-8	-6	411	386
-7	-6	328	334
-6	-6	449	433
-5	-6	133	117
-4	-6	132	142
-3	-6	285	297
-2	-6	621	628
-1	-6	474	458
0	-6	517	504
2	-6	498	490
3	-6	799	803
4	-6	342	389
5	-6	540	548
-8	-5	300	296
-7	-5	349	309
-6	-5	738	735
-5	-5	303	289
-4	-5	345	357
-2	-5	271	256
-1	-5	803	807
0	-5	1116	1110
1	-5	421	392
2	-5	725	726
3	-5	482	496
4	-5	176	192
5	-5	443	407
6	-5	155	165

Column group 5

H	K	FOBS	FCAL
-8	-4	334	298
-7	-4	187	147
-6	-4	584	562
-2	-4	304	284
-1	-4	213	262
0	-4	382	374
1	-4	291	273
2	-4	191	171
3	-4	271	268
5	-4	164	131
-10	-3	292	304
-9	-3	203	188
-8	-3	145	133
-6	-3	233	212
-5	-3	715	728
-4	-3	148	158
-3	-3	199	231
-2	-3	154	144
-1	-3	471	455
0	-3	583	569
1	-3	318	286
2	-3	207	223
3	-3	370	340
-10	-2	210	197
-9	-2	283	285
-7	-2	153	144
-5	-2	749	739
-4	-2	421	410
-3	-2	477	453
-2	-2	174	181
-1	-2	746	729
0	-2	1154	1169
1	-2	744	776
2	-2	220	231
4	-2	228	250
5	-2	309	319
-11	-1	315	288
-10	-1	202	149
-9	-1	163	133
-8	-1	180	210
-6	-1	230	228
-5	-1	542	515
-4	-1	399	396
-3	-1	332	342
-2	-1	467	429
0	-1	1096	1105
1	-1	774	768
2	-1	477	450
3	-1	252	263
4	-1	250	263
-11	0	317	362
-10	0	452	463
-9	0	632	620
-8	0	692	730
-7	0	467	452
-5	0	570	531
-4	0	805	822
-3	0	567	557
-2	0	786	775
-1	0	286	282
0	0	625	625
1	0	515	497
2	0	365	354
3	0	151	175
4	0	382	386
-11	1	222	237
-10	1	230	254
-9	1	273	273
-8	1	570	514
-7	1	1022	1052
-6	1	598	595
-5	1	243	243
-4	1	525	525
-3	1	707	721
-2	1	806	785
-1	1	473	456
0	1	195	192
1	1	360	371
2	1	270	290
3	1	235	211
4	1	304	312
-9	2	138	91
-8	2	310	334
-7	2	599	568

Table 8 (continued)

H	K	FOBS	FCAL
L = 5**			
-6	2	408	420
-5	2	231	226
-3	2	403	419
-2	2	371	373
-1	2	345	361
0	2	208	204
1	2	232	231
-9	3	179	156
-8	3	277	293
-7	3	390	389
-6	3	363	363
-4	3	324	307
-3	3	363	352
-2	3	405	415
-1	3	396	374
1	3	190	214
3	3	155	158
-10	4	260	265
-9	4	335	305
-7	4	407	409
-6	4	582	587
-5	4	300	313
-4	4	130	164
-3	4	268	289
-2	4	471	471
-1	4	667	687
0	4	292	274
-10	5	447	445
-9	5	404	438
-8	5	154	135
-7	5	451	461
-6	5	472	489
-5	5	200	192
-2	5	131	157
-1	5	567	624
0	5	148	127
1	5	298	356
-10	6	396	408
-9	6	499	513
-8	6	167	172
-7	6	417	415
-5	6	486	476
-4	6	271	283
-3	6	191	168
-1	6	361	367
-8	7	397	408
-7	7	210	279
-6	7	453	485
-5	7	309	325
-4	7	363	331
-3	7	389	389
L = 6**			
0	-10	241	248
1	-10	540	517
-4	-9	318	317
1	-9	210	235
3	-9	208	170
-4	-8	352	330
-3	-8	419	412
0	-8	356	356
1	-8	753	740
2	-8	692	672
4	-8	302	285
-7	-7	255	271
-5	-7	305	295
-4	-7	730	736
-3	-7	640	648
-2	-7	466	450
0	-7	325	314
1	-7	865	846
2	-7	754	738
3	-7	362	388
4	-7	165	139
-8	-6	295	225
-7	-6	406	410
-6	-6	380	392
-4	-6	380	389
-3	-6	661	666
-2	-6	578	585
-1	-6	227	259
1	-6	345	377
2	-6	588	604
3	-6	206	186
4	-6	205	178
-9	-5	391	360
-7	-5	220	250
-6	-5	623	602
-5	-5	396	358
-3	-5	508	502
-2	-5	326	318
-1	-5	509	517
0	-5	359	344
1	-5	281	253
2	-5	443	438
-7	-4	285	243
-6	-4	667	639
-5	-4	472	485
-3	-4	457	440
-2	-4	404	392
-1	-4	401	396
0	-4	288	300
1	-4	152	119
2	-4	289	331
-10	-3	194	156
-9	-3	238	272
-7	-3	150	30
-6	-3	613	614
-5	-3	563	538
-3	-3	366	328
-2	-3	429	438
-1	-3	328	345
0	-3	384	412
2	-3	179	258
-8	-2	164	157
-7	-2	214	177
-6	-2	644	613
-5	-2	650	597
-3	-2	545	526
-2	-2	311	303
-1	-2	221	222
0	-2	333	371
1	-2	286	321
-11	-1	184	187
-10	-1	242	223
-9	-1	322	314
-8	-1	301	309
-6	-1	407	388
-5	-1	690	677
-4	-1	694	658
-1	-1	762	755
0	-1	688	692
1	-1	451	479
-11	0	326	286
-10	0	512	496
-9	0	525	544
-8	0	472	461
-7	0	327	335
-6	0	499	543
-5	0	1011	1010
-4	0	867	859
-3	0	214	198
-2	0	226	258
-1	0	230	229
0	0	243	266
1	0	410	397
2	0	333	343
3	0	390	390
-11	1	328	316
-10	1	302	293
-9	1	392	382
-8	1	675	703
-7	1	365	359
-6	1	516	520
-5	1	580	573
-4	1	280	266
-3	1	218	236
-2	1	257	239
-1	1	389	400
1	1	273	262
2	1	192	201
-9	2	235	208
-8	2	472	439
-7	2	489	494
-5	2	155	220
-4	2	326	311
-3	2	226	212
-2	2	187	205
-1	2	172	201
1	2	192	187
-10	3	271	291
-8	3	340	321
-7	3	583	578
-5	3	283	279
-4	3	369	392
-3	3	210	206
-2	3	301	307
-1	3	166	143
1	3	150	175
-10	4	192	178
-9	4	189	173
-8	4	364	379
-7	4	276	288
-5	4	258	272
-4	4	208	241
-2	4	348	341
-1	4	415	392
-8	5	343	346
-7	5	509	487
-6	5	293	271
-3	5	171	234
-2	5	345	352
-8	6	276	240
-7	6	560	541
-6	6	445	420
-5	6	397	422
-4	6	339	354
L = 7**			
-4	-9	319	330
-1	-9	188	165
0	-9	431	395
1	-9	196	198
-5	-8	291	278
-4	-8	464	484
-2	-8	234	247
-1	-8	187	198
0	-8	231	243
1	-8	588	572
2	-8	485	452
-5	-7	454	453
-4	-7	682	673
-3	-7	509	512
-1	-7	232	233
0	-7	353	341
1	-7	709	684
2	-7	538	526
-8	-6	241	202
-7	-6	405	385
-6	-6	165	147
-5	-6	518	499
-3	-6	833	835
-2	-6	275	263
-1	-6	174	116
1	-6	357	358
2	-6	572	590
-8	-5	289	244
-7	-5	670	695
-6	-5	361	343
-4	-5	604	644
-3	-5	632	614
-2	-5	283	270
-1	-5	184	185
0	-5	164	140
2	-5	416	433
-9	-4	205	168
-7	-4	417	385
-6	-4	397	406
-4	-4	382	375
-3	-4	260	243
-2	-4	321	302
-1	-4	241	223
0	-4	283	274
2	-4	382	394
3	-4	164	165
-10	-3	268	269
-7	-3	326	300
-6	-3	426	447
-5	-3	245	264
-4	-3	179	189
-3	-3	191	199
-2	-3	303	268
-1	-3	228	193
0	-3	428	455
2	-3	203	180
3	-3	185	210
-10	-2	250	263
-9	-2	197	149
-7	-2	425	405
-6	-2	631	614
-5	-2	330	356
-4	-2	312	341
-3	-2	344	321
-2	-2	198	212
-1	-2	318	308
0	-2	451	417
1	-2	243	241
-10	-1	287	233
-9	-1	207	190
-7	-1	389	364
-6	-1	710	698
-5	-1	415	389
-4	-1	127	55
-2	-1	182	168
-1	-1	437	424
0	-1	501	495
1	-1	539	529
-10	0	526	559
-9	0	290	233
-8	0	373	353
-7	0	259	231
-6	0	768	744
-5	0	712	715
-4	0	371	366
-3	0	438	421
-1	0	233	216
0	0	490	478
1	0	616	602
-10	1	550	537
-9	1	367	295
-8	1	406	441
-6	1	511	451
-5	1	475	453
-4	1	449	449
-3	1	607	604
-2	1	455	442
0	1	302	293
1	1	401	442
-9	2	364	383
-8	2	437	421
-6	2	391	375
-5	2	322	342
-2	2	262	257
-1	2	190	184
0	2	182	157
-9	3	189	167
-8	3	217	220
-7	3	162	153
-5	3	195	198
-3	3	221	237
-2	3	342	309
-9	4	148	143
-8	4	272	228
-7	4	345	323
-5	4	248	251
-4	4	148	177
-3	4	294	285
-7	5	483	524
-6	5	206	150
L = 8**			
-4	-8	177	172
-2	-8	173	169
-1	-8	160	144
-6	-7	321	296
-5	-7	553	518
-4	-7	316	330
-2	-7	275	270
0	-7	213	239
-6	-6	294	285
-5	-6	592	576
-4	-6	564	599
-3	-6	248	227
1	-6	467	453
-8	-5	269	316
-7	-5	211	220
-5	-5	272	265
-4	-5	404	427
-3	-5	421	424
-2	-5	332	300
-1	-5	270	237
0	-5	245	227
1	-5	183	195
-7	-4	311	298
-6	-4	185	185
-5	-4	227	183
-4	-4	155	118
-3	-4	238	98
-2	-4	162	177
-1	-4	268	298
0	-4	299	331
-9	-3	167	31
-7	-3	183	197
-6	-3	270	252
-4	-3	197	166
-1	-3	302	311
-9	-2	252	276
-6	-2	335	315
-4	-2	167	186
-2	-2	192	192
-1	-2	502	478
0	-2	322	341
-9	-1	205	195
-7	-1	455	447
-6	-1	553	520
-5	-1	265	271
-2	-1	297	291
-1	-1	561	524
0	-1	604	598
-7	0	306	309
-6	0	649	608
-5	0	676	682
-4	0	439	455
-3	0	281	290
-1	0	497	482
-6	1	251	278
-5	1	364	327
-4	1	426	434
-3	1	403	389
-2	1	222	236
-7	2	171	178
-5	2	231	166
-3	2	282	268
-7	3	267	253
-5	3	289	253
L = 9**			
-5	-6	487	465
-4	-6	355	365
-3	-6	201	214
-5	-5	456	423
-4	-5	592	595
-3	-5	355	355
-2	-5	201	240
-6	-4	222	173
-3	-4	180	163
-2	-4	197	200
-6	-3	278	300
-3	-3	217	202
-8	-2	216	192
-7	-2	268	256
-6	-2	239	238
-5	-2	200	226
-4	-2	291	245
-3	-2	314	303
-2	-2	363	396
-8	-1	263	237
-7	-1	505	522
-6	-1	542	517
-5	-1	285	296
-3	-1	317	344
-7	0	264	245
-6	0	491	404
-5	0	493	442
-4	0	285	276

Table 9

Atomic Coordinates and Isotropic Temperature Factors for

the Unique Contents of the Unit Cell.

Atom	x	y	z	B *
Rh	0.09542(7)	-0.05735(7)	0.06606(9)	2.45
Cℓ1	0.1776(3)	0.0039(2)	0.3167(3)	4.17
P1	0.0670(3)	-0.2351(2)	0.0442(3)	2.95
P2	0.2648(3)	-0.0127(2)	0.0728(3)	3.03
O1	-0.0255(6)	-0.1164(5)	-0.1361(7)	2.67
O2	-0.0884(6)	-0.0928(5)	-0.0666(7)	2.86
C1	0.172(2)	0.255(2)	0.492(2)	10.33
Cℓ2	0.223(2)	0.377(1)	0.484(2)	8.7
Cℓ3	0.305(3)	0.367(1)	0.606(5)	20.3
Cℓ4	0.1238(8)	0.2598(5)	0.6050(8)	20.4

* These values are equivalent isotropic temperature
factors corresponding to the anisotropic thermal
parameters shown in Table 10

(Table continued)

Table 9 (continued)

(a) Phenyl Carbon Rigid Bodies

Name	x	y	z	B
Cl11	0.133(1)	-0.2670(8)	0.198(1)	3.1(3)
Cl12	0.0663(9)	-0.3343(6)	0.2282(9)	3.8(3)
Cl13	0.118(1)	-0.3600(6)	0.3448(7)	5.0(3)
Cl14	0.237(1)	-0.3183(8)	0.432(1)	4.5(3)
Cl15	0.3033(9)	-0.2510(6)	0.4019(9)	4.9(3)
Cl16	0.251(1)	-0.2253(6)	0.2853(7)	4.2(3)
D	4.210(4)	$x^{1\ddagger}$	0.1848(5)	
E	3.026(9)	$y^{1\ddagger}$	-0.2967(4)	
F	5.267(9)	$z^{1\ddagger}$	0.3151(5)	
Cl21	0.0960(7)	-0.3181(5)	-0.0827(8)	3.1(3)
Cl22	0.0727(6)	-0.2976(5)	-0.2031(9)	3.9(3)
Cl23	0.0996(7)	-0.3538(6)	-0.2989(6)	4.6(3)
Cl24	0.1498(7)	-0.4305(5)	-0.2742(8)	5.0(3)
Cl25	0.1731(6)	-0.4510(5)	-0.1538(9)	4.4(3)
Cl26	0.1462(7)	-0.3948(6)	-0.0581(6)	3.9(3)
D	2.712(4)	x^{1}	0.1229(4)	
E	1.647(5)	y^{1}	-0.3743(4)	
F	3.889(5)	z^{1}	-0.1785(5)	
Cl31	-0.0850(5)	-0.3020(7)	-0.0251(9)	2.8(2)
Cl32	-0.1318(7)	-0.2561(5)	0.0515(9)	4.1(3)
Cl33	-0.2434(8)	-0.3101(7)	0.0128(8)	5.4(3)
Cl34	-0.3083(5)	-0.4099(7)	-0.1026(9)	5.7(3)

(Table continued)

Table 9 (continued)

Name	x	y	z	B
C135	-0.2614(7)	-0.4557(5)	-0.1792(9)	5.9(3)
C136	-0.1498(8)	-0.4018(7)	-0.1405(8)	4.4(3)
D	0.680(4)	x^1	-0.1966(4)	
E	0.445(6)	y^1	-0.3559(4)	
F	0.198(6)	z^1	-0.0638(5)	
C211	0.3531(6)	0.1322(5)	0.1712(9)	3.1(3)
C212	0.4363(8)	0.1728(7)	0.1425(9)	4.4(3)
C213	0.5123(6)	0.2797(7)	0.2237(9)	5.2(3)
C214	0.5051(6)	0.3459(5)	0.3337(9)	5.0(3)
C215	0.4219(8)	0.3053(7)	0.3625(9)	5.2(3)
C216	0.3459(6)	0.1985(7)	0.2812(9)	3.9(3)
D	0.598(5)	x^1	0.4291(4)	
E	0.871(6)	y^1	0.2391(4)	
F	4.332(6)	z^1	0.2525(5)	
C221	0.241(1)	-0.0358(5)	-0.1031(9)	3.2(3)
C222	0.1490(9)	-0.0154(6)	-0.194(1)	4.4(3)
C223	0.1290(8)	-0.0268(6)	-0.328(1)	5.8(3)
C224	0.201(1)	-0.0584(5)	-0.3712(9)	6.3(4)
C225	0.2940(9)	-0.0788(6)	-0.281(1)	6.1(3)
C226	0.3140(8)	-0.0675(6)	-0.147(1)	4.5(3)
D	2.202(5)	x^1	0.2215(5)	
E	1.800(7)	y^1	-0.0471(4)	
F	3.215(8)	z^1	-0.2372(6)	

Table 9 (continued)

Name	x	y	z	B
C231	0.3710(7)	-0.0724(7)	0.1519(7)	3.3(3)
C232	0.3685(7)	-0.1722(6)	0.0755(8)	4.2(3)
C233	0.4474(8)	-0.2165(5)	0.143(1)	6.0(3)
C234	0.5289(7)	-0.1610(7)	0.2865(7)	6.0(3)
C235	0.5314(7)	-0.0611(6)	0.3629(8)	5.4(3)
C236	0.4524(8)	-0.0168(5)	0.296(1)	3.9(3)
D	2.879(5)	x^1	0.4499(4)	
E	2.434(5)	y^1	-0.1167(4)	
F	5.514(5)	z^1	0.2192(6)	

‡ These values represent the coordinates of the ring center of gravity.

(Table continued)

Table 9 continued

(b)   Phenyl Hydrogen Rigid Bodies

Name	x	y	z	B
H112	-0.019	-0.364	0.165	4.1
H113	0.070	-0.408	0.365	5.4
H114	0.274	-0.337	0.515	4.9
H115	0.388	-0.221	0.464	5.3
H116	0.299	-0.177	0.264	4.6
D	4.210			
E	3.026			
F	6.314			
H122	0.0371	-0.242	-0.221	4.3
H123	0.083	-0.339	-0.385	5.1
H124	0.169	-0.471	-0.343	5.5
H125	0.209	-0.506	-0.136	4.8
H126	0.163	-0.410	0.028	4.2
D	2.712			
E	1.647			
F	4.936			
H132	-0.085	-0.184	0.134	4.4
H133	-0.277	-0.277	0.068	5.9
H134	-0.388	-0.448	-0.130	6.3
H135	-0.308	-0.527	-0.262	6.5
H136	-0.116	-0.435	-0.196	4.8

Table 9 (continued)

Name	x	y	z	B
D	0.680			
E	0.444			
F	1.245			
H212	0.441	0.125	0.063	4.8
H213	0.572	0.309	0.203	5.7
H214	0.560	0.423	0.392	5.5
H215	0.417	0.353	0.441	5.7
H216	0.286	0.169	0.302	4.3
D	0.598			
E	0.871			
F	5.380			
H222	0.097	0.007	-0.162	4.8
H223	0.062	-0.012	-0.392	6.3
H224	0.187	-0.067	-0.468	6.9
H225	0.346	-0.101	-0.312	6.7
H226	0.380	-0.082	-0.082	4.9
D	2.202			
E	1.800			
F	4.262			
H232	0.310	-0.212	-0.028	4.6
H233	0.446	-0.288	0.088	6.6
H234	0.586	-0.193	0.335	6.6

Table 9 (continued)

Name	x	y	z	B
H235	0.590	−0.021	0.466	5.9
H236	0.454	0.055	0.350	4.3
D	2.879			
E	2.434			
F	6.561			

Table 10

Anisotropic Temperature Factors ($\overset{\circ}{A}{}^2 \times 10^3$)

Atom Name	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	33.4(7)	31.6(6)	31.0(7)	15.9(5)	16.6(5)	13.8(5)
P1	46(2)	35(2)	33(2)	20(2)	19(2)	15(2)
P2	38(2)	41(2)	35(2)	17(2)	16(2)	16(2)
Cℓ1	73(2)	52(2)	34(2)	29(2)	25(2)	17(2)
O1	33(5)	45(5)	31(5)	22(4)	16(4)	11(4)
O2	32(5)	34(5)	38(5)	19(4)	16(4)	19(4)
C1	180(20)	120(20)	70(10)	50(20)	70(20)	100(10)
Cℓ2	100(10)	120(10)	120(20)	46(8)	70(10)	37(8)
Cℓ3	240(30)	160(10)	450(50)	80(10)	250(30)	90(20)
Cℓ4	420(10)	129(5)	207(7)	21(6)	203(8)	22(5)

Table 11

Interatomic Distances

Atom 1	Atom 2	Distance($\mathring{A}$)	
Rh	P1	2.314(3)	2.316(3)*
Rh	P2	2.277(3)	2.281(3)*
Rh	Cℓ1	2.390(3)	2.402(3)*
Rh	O1	1.983(7)	
Rh	O2	2.198(7)	
Rh'	O1	2.778(7)	
Rh	O2'	2.069(7)	
P1	C111	1.815(7)	
P1	C121	1.829(7)	
P1	C131	1.829(7)	
P2	C211	1.833(7)	
P2	C221	1.821(8)	
P2	C231	1.832(7)	
O1	O2	1.44(1)	
Cl	Cℓ2	1.70(3)	
Cl	Cℓ3	1.80(3)	
Cl	Cℓ4	1.70(3)	

* Distance corrected for riding

Table 12

Selected Intramolecular Angles

Atom 1	Atom 2	Atom 3	Angle (°)
P1	Rh	P2	100.3(1)
P1	Rh	Cℓ1	90.6(1)
P1	Rh	O1	87.5(2)
P1	Rh	O2	92.5(2)
P1	Rh	O2'	169.4(2)
P2	Rh	Cℓ1	95.7(1)
P2	Rh	O1	106.2(3)
P2	Rh	O2	143.4(2)
P2	Rh	O2'	89.2(2)
Cℓ1	Rh	O1	158.0(3)
Cℓ1	Rh	O2	118.4(2)
Cℓ1	Rh	O2'	93.4(2)
O1	Rh	O2	39.9(3)
O1	Rh	O2'	85.2(3)
O2	Rh	O2'	76.9(3)
Rh	P1	C111	121.3(3)
Rh	P1	C121	115.5(3)
Rh	P1	C131	107.4(3)
Rh	P2	C211	114.5(3)
Rh	P2	C221	110.7(3)
Rh	P2	C231	120.6(3)
Cℓ2	C1	Cℓ3	47. (1)

(Table continued)

Table 12 (continued)

Atom 1	Atom 2	Atom 3	Angle (A°)
Cℓ2	Cl	Cℓ4	116. (1)
Cℓ3	Cl	Cℓ4	100 (1)
O1	O2	Rh'	103.4(5)
O1	O2	Rh	61.7(4)
Rh	O2	Rh'	103.0(3)

Table 13

Selected Intramolecular Non-Bonded Contacts

Atom 1	Atom 2	Distance (Å)
Rh	Rh'	3.340(2)
Rh	H222	2.98
O2	O2'	2.65(1)
H132	H222'	2.40
H216	O2'	2.62
H122	O1	2.25
H222	O1	2.33
H132	O2	2.88
H216	Cℓ1	2.56
H215	Cℓ3	2.91
O1	O1'	3.49(1)
O1	O2'	2.75(1)

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Table 14

Selected Intermolecular Contacts

Atom 1	Atom 2	Symmetry Operation (on atom 2)	Distance(Å)
H115	H236	$\bar{x}+1,\ \bar{y},\ \bar{z}+1$	2.43
H223	H223	$\bar{x},\ \bar{y},\ z-1$	2.46
H115	H336	$\bar{x}+1,\ \bar{y},\ \bar{z}+1$	2.43

Fig. 5

A General View of, $[(O_2)RhC\ell(P(C_6H_5)_3)_2]_2$
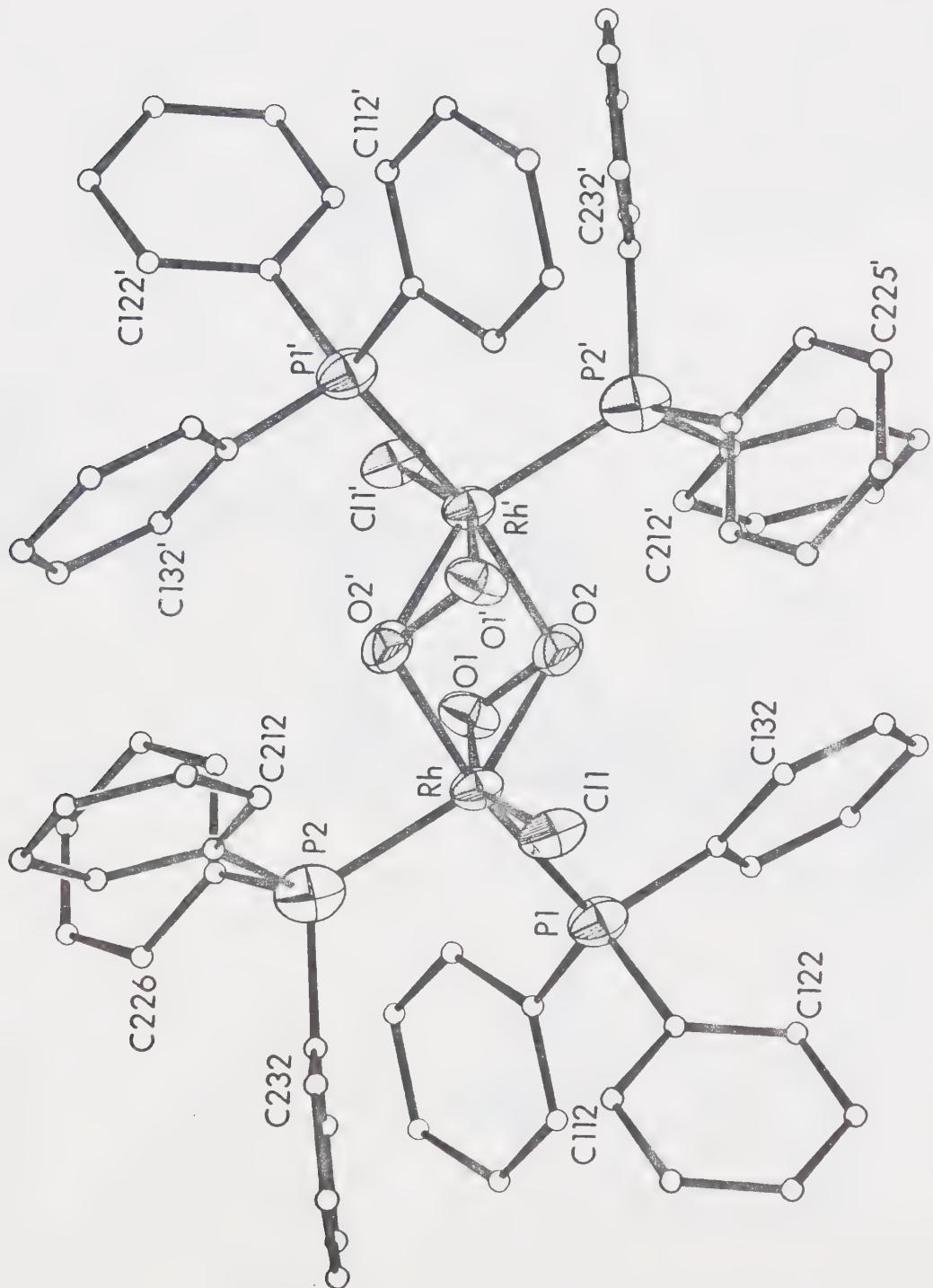
Fig. 6

Dioxygen Bridging Geometry
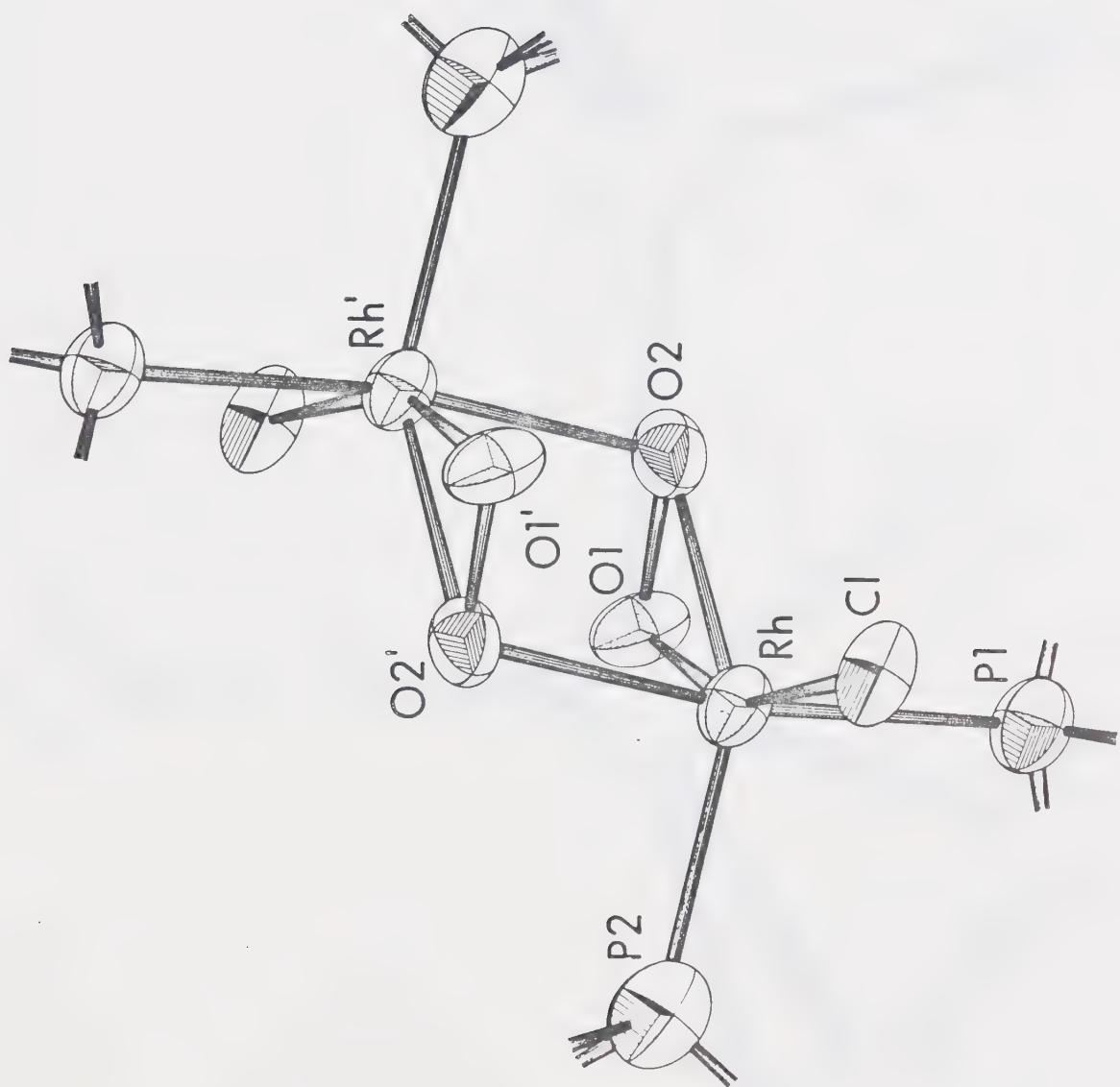
Fig. 7

Subunit Viewed down P1-O2' Direction
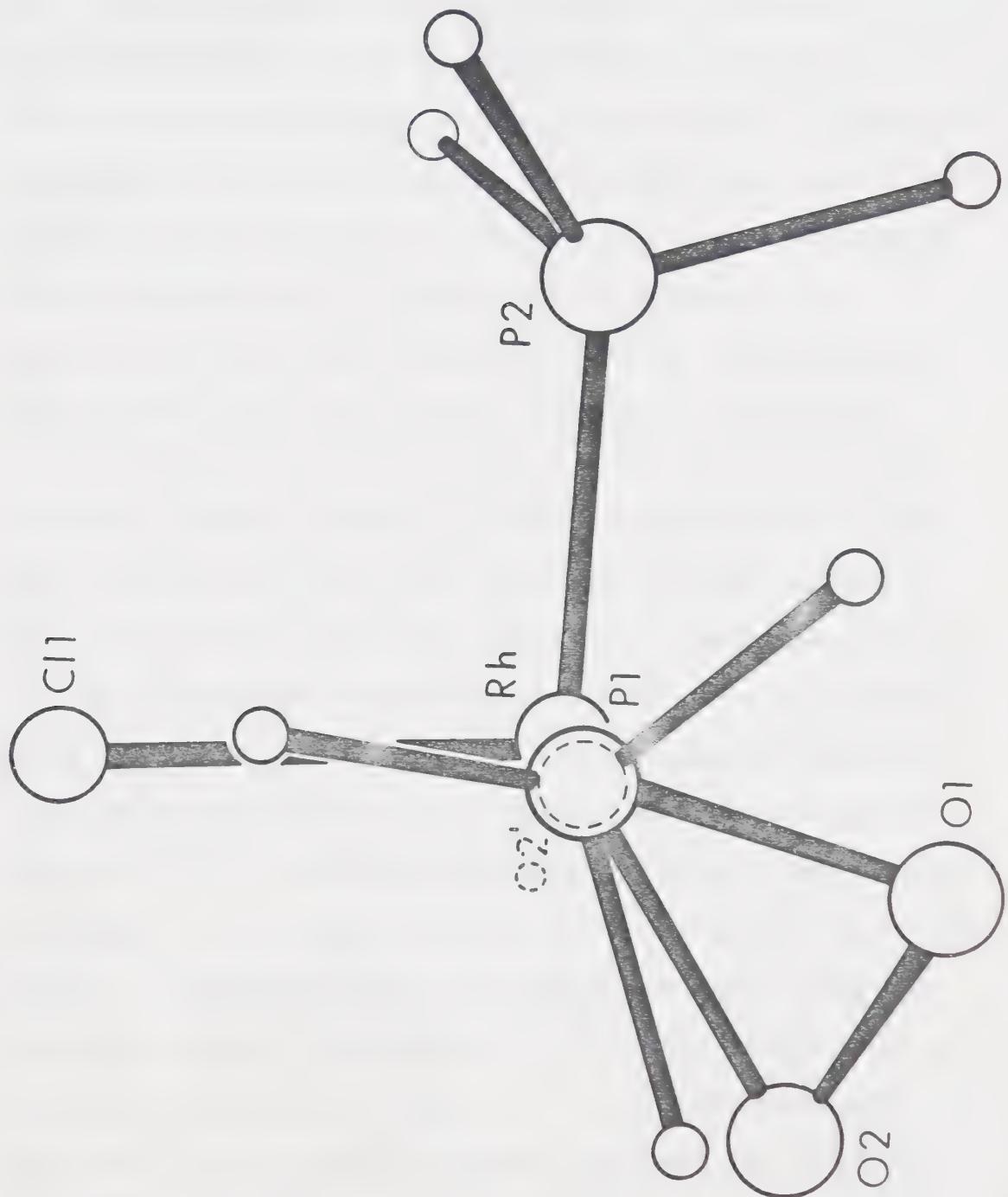
Discussion

The structure (Fig. 5) was found to contain dimeric units, situated at inversion centers in the unit cell. The methylene chloride molecule is situated at least 5.6 Å from the central coordination sphere and thus is in no way coordinated to the rhodium atoms. The over-all geometry of each subunit can be described as a distorted trigonal bipyramid assuming that the coordinated dioxygen molecule is considered to occupy a single co-ordination site. The rhodium atoms obey the effective atomic number rule and are coordinatively saturated.

Five coordinate dioxygen species are not particularly unusual (Table 3), however the manner in which this compound achieves this geometry is most unexpected and quite novel. The three equatorial positions of the trigonal bipyramidal subunit are occupied by a triphenylphosphine, a chlorine atom and the coordinated dioxygen molecule in keeping with the similar iridium dioxygen complexes [17-19] (also containing equatorially coordinated dioxygen). The axial coordination sites are occupied by another triphenylphosphine and an oxygen atom from the dioxygen molecule coordinated to the rhodium related by the inversion center. Thus the coordinated dioxygen molecules act as bridging ligands between the rhodium atoms (Fig. 6), with one oxygen atom of each molecule being coordinated in the usual manner for a π-bonded di-

atomic ligand, whereas the other atom although posessing a similar geometric arrangement is also able, *via* a third bond to bridge the two rhodium atoms.

The previously known π-bonded dioxygen derivatives of Vaska's compound and its analogues [33] contain similar geometry but not the bridging bond, whilst O_2F_2 [81] and some of the dioxygen bridged cobalt complexes [97-100] contain fairly similar peroxo symmetry to the bridge without the π-geometry.

In the purely π-bonded dioxygen species dioxygen molecules are situated so that the metal-oxygen distances are equivalent (although some of these complexes [18,19] are disordered and thus any differences in these distances would have been impossible to detect). This is not the case in this complex as the two rhodium-oxygen bond lengths within the same subunit, (Rh-O1, 1.973(7); Rh-O2, 2.195(7) $\overset{o}{A}$) are significantly different. The shorter bond is between the rhodium atom and the oxygen not participating in bridging. The rhodium-oxygen distances to the symmetry related subunit are: (Rh$'$-O1, 2.778(7); Rh$'$-O2, 2.069(7) $\overset{o}{A}$). These values indicate that the dioxygen molecules are not perpendicular to the rhodium-rhodium vector as for example had been postulated originally by Vannerberg and Brosset [79] for the structure of $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$. The rhodium-rhodium distance is 3.340(2) $\overset{o}{A}$ and thus is too

long for a metal-metal bond [117,118]. Discussion of the rhodium-phosphorus and rhodium-chlorine bond lengths, which appear normal, is deferred until Chapter VI.

Using the conventional molecular orbital scheme for dioxygen in the coordinated state [46], the dioxygen molecule may be considered as having the initial configuration $\pi^{*2}\pi^{*0}$ instead of the usual paramagnetic ground state with two unpaired electrons ($\pi^{*1}\pi^{*1}$). The bonding within the fragment RhO1O2 could then be described (according to Griffith [64]) as involving a donation from the ligand to the metal from a fully occupied π-orbital accompanied by back donation from the metal to the empty dioxygen π^* orbital. This model has been widely used to explain a large variation in dioxygen bond lengths. The greater the amount of back donation, the longer the expected oxygen-oxygen bond length would be, assuming either: (1) a fairly constant ligand-metal donation, or (2) the normal synergic interaction [18]. Thus the iridium complexes [17,19] with variations in the oxygen-oxygen bond lengths of from 1.30(3) Å to 1.66(3) Å could be viewed as containing a superoxide ion (O_2^-) in the first case and a peroxide ion (O_2^{2-}) in the second. These increases in bond length would be expected from a simple bond-order calculation.

The retention of Griffith's model seems desir-

able for this complex and the bridging nature of the
dioxygen ligand may be explained by observing that the
filled π* orbital (of the dioxygen ligand) not taking
part in overlap with the first rhodium atom would be
perpendicular to the RhO1O2 plane and thus in a position
favourable for the formation of a σ-bond to the neighbouring
rhodium. The observed angles of 103.4(5)° for O1O2Rh'
and 103.0(3)° (RhO2Rh') seem reasonable when the electron
density plots for the molecular orbitals of dioxygen [49]
are considered. This particular model could accommodate
a wide range of O1O2Rh' angles as it is possible for the
filled π-orbitals of the dioxygen to also donate electrons
to the second rhodium atom and the observed angle could
be considered as a compromise between the two possible
bonding extremes.

It is interesting that a *bis*-chloro bridged
species (structure 1) does not form even though it might
appear equally feasible.
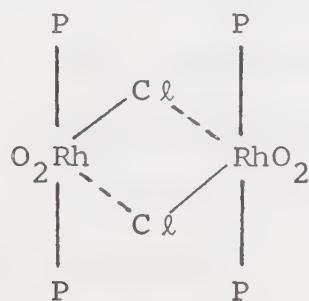
1

The preference for the dioxygen bridge suggests that there is a particularly suitable energy relationship between the occupied π^* orbital of the dioxygen molecule and the dz^2 orbital of the rhodium atom (the "z" axis being defined as the pseudothreefold rotation axis of the trigonal bipyramidal subunit). This is supported by the chemical behaviour of the complex as it is inert to either strong acid or base.

The bonding description does not allow a detailed discussion of the oxygen-oxygen bond length as π^* donation to the neighbouring rhodium would decrease the oxygen-oxygen bond length whereas π as a donor would have an opposing effect. In addition the back donation from the metal to the empty π^* orbital could vary. Comparisons with the similar complex $[(O_2)RhCl(P(C_6H_5)_3)_3]$ should prove meaningful and these are made in Chapter IV.

An alternate method of describing the structure of $[(O_2)RhCl(P(C_6H_5)_3)_2]_2$ would be to consider the rhodium as Rh(III) and the dioxygen molecule as a chelating peroxide ion, the bridges being formed from one of the lone pairs of one oxygen atom of each peroxide ion. This could then be viewed as partially analogous to the bent dioxygen cobalt species [65] containing only a π^* donor bond as discussed in Chapter I.

The steric requirements of triphenylphosphine have been discussed by Tolman [119]. The wide Tolman angle

of 145 $\pm$ 2 for a single ligand suggests that a *cis* pair of triphenylphosphines (P1-Rh-P2, 100.2(1)°) would have to be interlocked. The hydrogen-hydrogen non-bonded contacts (Tables 13 and 14) are all longer than the sum of their van der Waals radii [120]. A number of other close intra-molecular contacts were observed (Cℓ1-H216, 2.56; O1-H122, 2.25; O1-H222, 2.33; Rh-H222, 2.98 Å) with the closest intramolecular chlorine-hydrogen contact (Cℓ1-H224(x,y,z+1)) being 2.84 Å. The chlorine-hydrogen contacts are similar to those found in the structure of $RhCℓ(CS)(P(C_6H_5)_3)_2$ [121]. All contacts are not believed to represent any attraction, but rather to reflect the difficulty of accomodating two bulky ligands in a mutually *cis* arrangement.

The geometry of the methylene chloride molecule is in acceptable agreement with literature values [122,123] despite the deficiencies in the model. The molecule does not appear to be coordinated in any way to the rhodium complex.

The dimeric species reported here cannot represent the major species present in solution as indicated by its insolubility. When oxygen is passed through solutions of $RhCℓ(P(C_6H_5)_3)_3$ the formation of the dioxygen dimer from the $(O_2)RhCℓ(P(C_6H_5)_3)_2$ monomer would be expected to be a slow reaction in view of the highly specific geometry required.

A nitroso complex $[Fe(CO)_3(N\ O)(C_6H_5)]_2$ [125] (2)

published at the same time as the dioxygen dimer [126] has certain similarities in structure.
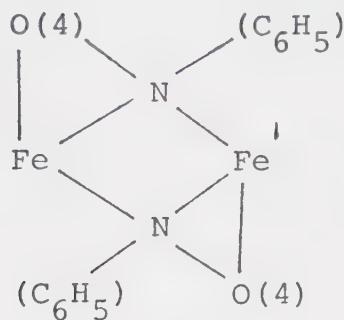
2

The nitroso group is located with the nitrogen atom bonded in an analogous manner to the dioxygen dimer O2 atom. The geometry of the nitrosyl group is interesting as the iron-oxygen distances of 1.91(1) Å and 2.73(1) Å plus the two angles (Fe-N-Fe', 103.1(3)° and Fe-N-O(4), 104.6(5)°) closely resemble the equivalent values in the dioxygen complex. The geometries are thus extremely similar except for the expected differences in interatomic bond lengths and the equality of the two iron-nitrogen distances (Fe-N, 2.02(1); Fe'-N, 1.98(1) Å). No detailed bonding explanations were given. Other possibly similar dioxygen species are $Rh(P(C_6H_5)_3)_3O_2$ [127] which is diamagnetic, explosive and probably dimeric and $[(O_2)M(tert-BuNC)_2]_n$ [78], M = Ni, Pd. The latter polymeric species was postulated from highly unreliable data.

Further comparisons of the *bis*-phosphine

dioxygen dimer with other similar complexes are included in Chapter IV and similarities to the parent complex $RhCl(P(C_6H_5)_3)_3$ are examined in Chapter VI.

CHAPTER IV

The Crystal and Molecular Structures of

$$[(O_2)RhC\ell(P(C_6H_5)_3)_3 \cdot 2CH_2C\ell_2]$$

Experimental

Crystals of $(O_2)RhC\ell(P(C_6H_5)_3)_3$ were prepared according to the method described in Chapter II. They were examined under a microscope and found to be yellow needles, usually arranged in clusters. After considerable searching a single crystal was found and cut to the desired length of approximately 0.2 mm. This crystal was then mounted on the end of a thin glass fibre so that the needle axis was coincident with the rotation axis of the goniometer head.

Examination of preliminary Weissenberg and precession photographs indicated that the crystal possessed orthorhombic symmetry. The systematic absences (hk0, h = 2n + 1; h0ℓ, ℓ = 2n + 1; 0kℓ, k = 2n + 1) were consistent with the unique choice of the space group *viz* Pbca. The crystal was mounted on a Picker manual diffractometer so that the "b" axis (needle axis) was coincident with the diffractometer ϕ axis. Precise lattice parameters and their estimated standard deviations were determined as a, 24.817(4); b, 18.359(2); c, 23.200(4) Å from the setting angles of twelve accurately centered high angle reflections at 22°C. All peaks showed good

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resolution of the $K\alpha_1$, $K\alpha_2$ doublet and only the α_1 peaks (λ, 1.54051 Å) were used. The density of the complex was determined by the flotation method in aqueous potassium iodide as ρ_{obs}, 1.411 g-cm^{-3} which is in excellent agreement with the calculated density of 1.416 g-cm^{-3} assuming eight formula units per unit cell. There are consequently no restrictions on the position or orientation of the formula unit in this space group since the number of general positions is eight.

A careful examination of peak profiles showed no obvious physical defects in the study crystal. Intensity data were collected with copper $K\alpha$ X-radiation using the coupled $\omega/2\theta$ method with a 2° takeoff angle. The diffractometer was equipped with a graphite crystal monochromator (002 reflecting plane). Each data point was scanned from $(2\theta - 1)°$ to $(2\theta + 1)°$ with a scan speed of 2° per minute. Background counts were estimated from a linear interpolation of 30 second stationary counts taken at the limits of the scan. During the data collection, the intensities of six reflections were monitored at periodic intervals to allow for correction of crystal decomposition and to detect crystal misalignment. Data were only measured to 80° in 2θ as indicated by the preliminary photography. Data collection was terminated after 1755 reflections for this first crystal when the standard reflections had decreased in intensity by 10 - 20%.

The crystal faces were identified as the forms { 100},
{010} and {001}, and the perpendicular distances between
the opposite members of each form were measured as
0.010, 0.028 and 0.018 cm respectively. The variation
in intensity of the 0k0 reflections with the setting angle
ϕ was measured to provide experimental evidence for the
correctness of subsequent absorption corrections. A
second crystal of the same habit and with dimensions
(0.008 x 0.009 x 0.032 cm), was used to collect the
remaining 1970 reflections. The variation of I_{0k0} with
ϕ was studied for this second crystal. All intense ref-
lections with count rates in excess of 10^4 counts per
second were remeasured under conditions such that the
scattered X-rays did not exceed the linear response range
of the scintillation counter.

Finally, representative reflections from the
first crystal were remeasured with the second crystal to
improve the merging of the two data sets. Both crystals
appeared to have similar rates of decomposition (directly
proportional to $\sin \theta / \lambda$ and logarithmically related to
time) and only decomposed when exposed to X-rays. Of the
total 3745 reflections measured, 2073 were found to be
statistically reliable using the criterion $I < 3$.
Decomposition and absorption corrections were then
applied ($\mu = 62.1 \text{ cm}^{-1}$) with the transmission factors
varying from 0.517 to 0.637 in the first crystal and from

0.356 to 0.544 in the second. The data were then corrected for Lorentz and polarization effects and the derived structure amplitudes and their standard deviations calculated (p = 0.03) after the two data sets had been scaled.

Solution of Structure and Refinement

A Patterson map was calculated and the atomic coordinates of the rhodium atom found from the Harker line peaks [128] (Table 15). As the "y" and "z" coordinates were approximately 0.25, a large number of peaks were superimposed. Although some evidence of the chlorine was found, only the rhodium atom was included in the first cycle of refinement (R_1, 0.547). The positions of the chlorine atom Cℓ1 and the three phosphorus atoms were located from an electron density map calculated at this point. The rest of the molecule was found as outlined in Table 16.

The carbon rings were constrained to D_{6h} symmetry, with carbon-carbon bond lengths of 1.392 Å, to minimize the number of parameters. The temperature factors of all atoms were not refined until R_1 = 0.178 (Table 17) as unrealistic values were obtained before all atoms were included. The values used (Rh, Cℓ, P; 2.5; C, 5.0) were similar to the final equivalent isotropic temperature factors obtained for the dimeric species

(Chapter III). The atomic scattering factors for rhodium, chlorine, phosphorus and carbon atoms were those of the neutral atoms and included the real and imaginary terms for anomalous dispersion for the rhodium, chlorine and phosphorus atoms. These scattering factors were obtained from Cromer's coefficients [111]. Hydrogen atoms were included at their calculated positions with carbon-hydrogen bond lengths of 1.0 $\overset{\circ}{A}$ and isotropic thermal parameters set 10% larger than those of the carbon atoms to which they were attached. The hydrogen scattering factors were those of Mason and Robertson [113].

Refinement was considered complete when the maximum parameter shift was one seventh of the corresponding standard deviation. The standard deviation of an observation of unit weight was 1.79 at convergence, which is reasonable in view of the constraints imposed upon the model. A final electron density difference map was calculated and the largest positive and negative peaks (0.38 and -0.36 e.$\overset{\circ}{A}^{-3}$; cf carbon ~3e.$\overset{\circ}{A}^{-3}$) were located near the methylene chloride molecules.

Table 15

Assignment of Patterson Map Peaks

Peak Coordinates			Rel. Height (origin=999)	Assignment	Calc. Height	Calc. Coordinates (from Solution)		
u	v	w						
0.168,	0.500,	0.500	174	1/2-2x,1/2,1/2	159	0.168,	0.500,	0.500
-0.168,	0.500,	0.500	180	1/2+2x,1/2,1/2	159	-0.168,	0.500,	0.500
0.00,	0.00,	0.00		0,1/2+2y,0	159	0.0,	-0.030,	0.0
..,	..,	..		0,1/2-2y,0	159	0.0,	0.030,	0.0
0.504,	0.00,	0.00	384	1/2,0,1/2+2z	159	0.500,	0.00,	-0.026
..,	..,	..	(total)	1/2,0,1/2-2z	159	0.500,	0.00,	0.026
..,	..,	..		1/2,1/2+2y,1/2+2z	79	0.500,	-0.030,	-0.030
..,	..,	..		1/2,1/2-2y,1/2+2z	79	0.500,	0.030,	-0.030
..,	..,	..		1/2,1/2+2y,1/2-2z	79	0.500,	-0.030,	0.030
..,	..,	..		1/2,1/2-2y,1/2-2z	79	0.500,	0.030,	0.030
0.324,	0.500,	0.500	128	2x,1/2,2z	79	0.332,	0.500,	0.474
..,	..,	..		2x,1/2,2$\bar{z}$	79	0.332,	0.500,	0.526

(Table continued)

Table 15 continued

Peak Coordinates			Rel. Height (origin=999)	Assignment	Calc. Height	Calc. Coordinates (from Solution)		
u	v	w						
..	..	..		$2x, 2y, 2z$	40	0.332,	0.470,	0.474
..	..	..		$2x, 2y, 2\bar{z}$	40	0.332,	0.470,	0.526
..	..	..		$2x, 2\bar{y}, 2z$	40	0.332,	0.520,	0.474
..	..	..		$2x, 2\bar{y}, 2z$	40	0.332,	0.530,	0.526

rhodium solution $x = 0.166$, $y = 0.235$, $z = 0.237$

Table 16

Structure Solution Sequence

Refinement Cycle	Atoms used in Refinement	R_1	Atoms found in Diff. Map
1	Rh	0.547	Cℓ1,P1,P2,P3
2	Rh,Cℓ1,P1,P2,P3	0.439	O1,O2,Cℓ2,Cℓ3,Cℓ4,Cℓ5,C111-C116, C121-C126,C311-C316
3	Rh,Cℓ1,P1,P2,P3,O1,O2,Cℓ2, Cℓ3,Cℓ4,Cℓ5,C111-C116, C121-C126,C311-C316	0.406	
4	..	0.305	C131-C136,C211-C216,C221-C226
5	Rh,Cℓ1,P1,P2,P3,O1,O2,Cℓ2, Cℓ3,Cℓ4,Cℓ5,C111-C116,C121- C126,C131-C136,C211-C216, C221-C226,C311-C316	0.243	C231-C236,C321-C326,C331-C336, C1,C2
6	Rh,Cℓ1,P1,P2,P3,O1,O2,Cℓ2, Cℓ3,Cℓ4,Cℓ5,C1,C2,C111-C116, C121-C126,C131-C136,C211-C216 C231-C236,C311-C316,C321-C326, C331-C336	0.178	

Table 17

Structure Refinement Sequence

Refinement Cycle	Model	R_1	R_2
6	All atoms included, isotropic temperature factors held constant	0.178	0.242
7	Temperature factors refined	0.111	0.134
8	Anomalous dispersion correction	0.092	0.109
9	Central atoms given anisotropic thermal parameters	0.073	0.087
10	Hydrogen atoms included	0.060	0.072
11	.. .. ..	0.053	0.064
12	.. .. ..	0.049	0.059

Results

Table 18 gives the observed ($|F_o|$) and cal-
culated ($|F_c|$) structure amplitudes (electrons x 10).
The final atomic coordinates of all atoms are included
in Table 19 with the anisotropic thermal parameters
(U_{ij}) of the central atoms listed in Table 20. Other
tables give the interatomic distances (Table 21), inter-
atomic angles (Table 22) and inter- and intramolecular
non-bonded contacts (Tables 23 and 24 respectively) with
the standard deviations (as calculated by ORFFE II) of
the least significant digit included in parentheses.
Bond lengths from the rhodium atom to the ligand atoms
were also calculated to include a correction for thermal
motion in which the second or lighter atom was assumed to
ride on the heavier rhodium.

Fig. 8 shows a general view of the molecule
with views down the P1-P3 and Rh-P2 directions (Figs. 9
and 10 respectively) being included.

Table 18

Observed and Calculated Structure Amplitudes

(electrons x 10)

Column group 1

H	K	FOBS	FCAL
L = 0			
2	0	3692	4087
4	0	879	1020
6	0	1673	1816
8	0	2728	2880
10	0	4100	4236
12	0	1798	1830
14	0	1994	2098
2	1	4908	5474
4	1	524	505
6	1	3444	3690
8	1	4115	4327
10	1	3349	3468
12	1	1176	1289
14	1	613	662
16	1	1769	1706
20	1	749	481
0	2	7737	8371
2	2	3122	3278
4	2	395	373
6	2	1171	1145
8	2	3109	3310
10	2	1232	1040
12	2	3084	3003
14	2	483	474
2	3	2843	3131
4	3	5738	5984
6	3	1106	1164
8	3	1076	967
10	3	2403	2490
12	3	401	364
14	3	523	515
20	3	917	1218
0	4	3892	3774
2	4	1053	1007
4	4	3797	3907
6	4	2554	2646
8	4	513	495
10	4	445	420
12	4	2945	2933
16	4	654	726
2	5	2208	2283
4	5	2239	2329
6	5	653	691
8	5	1891	1967
10	5	1457	1550
12	5	1228	1280
14	5	671	677
0	6	5150	5031
2	6	603	605
4	6	1268	1326
6	6	1678	1607
8	6	1529	1502
10	6	377	269
12	6	3705	3657
14	6	2343	2399
18	6	535	727
2	7	2330	2419
4	7	4262	4266
6	7	1673	1646
8	7	1851	1899
10	7	2574	2548
14	7	1354	1391
16	7	1305	1196
0	8	1282	1302
2	8	1336	1401
4	8	1550	1520
6	8	700	678
8	8	1187	1201
10	8	550	492
12	8	2175	2222
14	8	1566	1549
2	9	1572	1614
4	9	2949	2905
6	9	355	199
10	9	720	741
12	9	624	606
16	9	729	762
2	10	751	710
4	10	413	225
6	10	867	872
8	10	859	802
14	10	532	363
2	11	574	611
4	11	581	704
8	11	1245	1192
10	11	669	725
12	11	674	643
14	11	623	551
0	12	1242	1197
4	12	526	294
6	12	1259	1281
2	13	825	648
4	13	1661	1650
8	13	1431	1352
0	14	616	675
2	14	1109	1077
4	14	860	784
6	14	1258	1328

Column group 2

H	K	FOBS	FCAL
4	15	615	595
L = 1			
1	1	171	295
2	1	557	599
3	1	307	252
4	1	576	530
5	1	1347	1412
6	1	3164	3278
8	1	310	297
10	1	1175	1147
13	1	302	399
14	1	343	321
15	1	489	606
16	1	1183	1176
0	2	1476	1595
1	2	179	66
2	2	218	164
3	2	1229	1155
4	2	325	342
5	2	986	1007
6	2	808	786
7	2	2797	2965
8	2	1991	2147
9	2	317	278
12	2	747	721
14	2	812	883
15	2	466	592
16	2	677	718
1	3	831	749
2	3	1134	1143
3	3	1173	1126
5	3	2481	2470
6	3	614	584
7	3	1474	1566
8	3	456	483
9	3	513	656
10	3	1331	1357
12	3	723	605
13	3	396	444
14	3	366	269
15	3	387	355
16	3	525	597
17	3	585	639
20	3	796	838
0	4	1988	2072
1	4	1287	1355
2	4	726	691
3	4	462	575
4	4	561	554
5	4	1529	1577
6	4	614	652
7	4	1095	1146
8	4	1101	1077
9	4	341	260
10	4	304	323
11	4	540	675
12	4	1042	1025
15	4	617	716
18	4	484	499
1	5	247	137
3	5	1641	1717
4	5	1161	1206
5	5	345	344
6	5	384	371
8	5	620	654
9	5	1293	1255
10	5	542	617
11	5	313	379
12	5	507	533
14	5	373	316
0	6	983	1000
1	6	640	613
3	6	921	934
5	6	1701	1763
6	6	1088	1078
7	6	710	695
8	6	301	197
10	6	1983	1918
11	6	573	590
12	6	1650	1720
13	6	1027	1054
18	6	591	451
1	7	891	930
2	7	1726	1663
3	7	599	619
4	7	770	705
6	7	819	815
8	7	1247	1188
10	7	1217	1278
12	7	513	646
14	7	823	792
0	8	2772	2737
2	8	2151	2092
4	8	971	964
5	8	911	898
6	8	602	769
7	8	375	439
8	8	1813	1849

Column group 3

H	K	FOBS	FCAL
11	8	489	502
12	8	2776	2794
14	8	750	686
1	9	348	345
2	9	2018	2038
3	9	611	554
4	9	1598	1590
6	9	785	805
8	9	1371	1381
10	9	2234	2299
11	9	524	548
14	9	1594	1560
16	9	574	478
0	10	1878	1856
1	10	344	321
2	10	1482	1432
3	10	611	600
4	10	610	531
6	10	699	720
7	10	356	310
8	10	707	720
10	10	1115	1147
12	10	2669	2562
2	11	1378	1396
4	11	802	832
5	11	765	641
8	11	792	914
10	11	1116	1140
14	11	1155	1190
0	12	1338	1400
1	12	533	532
4	12	724	679
6	12	601	508
10	12	1707	1698
11	12	563	386
12	12	1017	1037
2	13	900	831
8	13	1374	1427
10	13	746	761
0	14	1522	2074
2	14	785	878
3	14	529	385
6	14	913	1007
2	15	1108	1066
L = 2			
0	0	7161	8020
1	0	909	816
2	0	2296	2200
3	0	439	359
4	0	278	372
6	0	6927	7018
7	0	1878	1661
8	0	2659	2745
9	0	2468	2569
10	0	3953	3972
11	0	516	503
12	0	3312	3443
14	0	1499	1337
15	0	617	577
18	0	1273	1299
20	0	869	1062
1	1	168	162
2	1	4482	4480
3	1	937	958
4	1	732	709
5	1	1096	1127
6	1	1334	1376
7	1	1458	1427
8	1	1844	1854
9	1	1901	1965
10	1	4000	4059
14	1	2296	2294
15	1	599	646
16	1	1336	1292
20	1	1060	1139
0	2	5480	5698
1	2	221	140
2	2	1628	1630
3	2	1157	1171
4	2	739	696
5	2	572	603
6	2	2002	2476
7	2	664	743
8	2	567	447
9	2	635	796
10	2	2665	2699
11	2	1471	2263
12	2	2573	2732
13	2	563	525
14	2	1213	1175
18	2	678	761
0	3	330	255
3	3	4712	4609
3	3	504	565
4	3	1012	1084
5	3	1076	1130
6	3	471	515
7	1	634	800
8	3	1647	1559

Column group 4

H	K	FOBS	FCAL
10	3	1897	1904
11	3	687	738
12	3	814	825
13	3	1789	1890
14	3	949	1069
0	4	3398	3358
1	4	423	403
2	4	1991	1980
4	4	639	618
5	4	411	481
6	4	1382	1374
7	4	1724	1783
8	4	925	934
9	4	2211	2305
10	4	1073	1105
11	4	1670	1694
12	4	2035	2000
14	4	629	645
16	4	617	509
18	4	812	836
1	5	677	667
2	5	2247	2302
3	5	585	548
4	5	959	916
5	5	280	319
6	5	579	561
7	5	1051	1046
8	5	1092	1097
9	5	316	309
10	5	2384	2335
11	5	1075	1064
12	5	494	516
14	5	1174	1180
16	5	669	636
0	6	2359	2252
1	6	1245	1207
2	6	2575	2576
3	6	360	350
4	6	815	819
6	6	3536	3580
7	6	334	323
8	6	1345	1481
9	6	785	695
10	6	823	797
11	6	486	437
12	6	1388	1358
14	6	823	765
17	6	591	552
18	6	1117	1196
1	7	625	571
2	7	3768	3758
4	7	2766	2784
8	7	880	966
9	7	255	320
7	7	2545	2490
11	7	477	517
12	7	700	693
13	7	464	168
14	7	1603	1502
15	7	573	446
16	7	1113	1062
0	8	422	437
2	8	1743	1703
3	8	746	717
6	8	1359	1504
7	8	567	528
8	8	579	611
9	8	533	491
10	8	968	984
12	8	1436	1433
14	8	1268	1108
1	9	715	677
2	9	1350	1314
3	9	660	607
4	9	1715	1740
6	9	815	825
8	9	695	700
10	9	1181	1211
14	9	928	848
16	9	554	594
0	10	1619	1647
2	10	830	738
6	10	627	694
10	10	621	812
2	11	596	552
3	11	325	180
4	11	840	773
6	11	964	845
0	12	403	444
2	12	610	586
6	12	1934	1705
2	13	743	761
4	13	1346	1345
8	13	785	818
10	13	577	569
2	14	1254	992
6	14	1537	1521
9	14	642	569
L = 3			

Column group 5

H	K	FOBS	FCAL
1	1	182	229
2	1	1569	1512
3	1	786	745
4	1	1628	1587
5	1	263	144
6	1	1300	1314
7	1	537	566
10	1	593	605
11	1	1042	999
0	2	1283	1238
1	2	1592	1546
2	2	252	289
3	2	1053	1053
4	2	4657	4627
5	2	2334	2307
6	2	1377	1405
7	2	886	858
8	2	1455	1394
10	2	397	358
11	2	403	351
12	2	1213	1247
13	2	1076	967
15	2	1052	1072
18	2	588	707
20	2	794	906
1	3	752	725
2	3	364	281
3	3	1904	1953
4	3	1716	1662
7	3	730	738
8	3	1430	1416
10	3	1688	1650
14	3	769	-798
15	3	400	413
20	3	531	585
0	4	276	262
1	4	519	505
2	4	970	1002
3	4	1030	1023
4	4	1507	1530
5	4	1590	1579
6	4	430	450
7	4	909	872
10	4	733	746
11	4	608	570
12	4	1359	1269
15	4	491	561
17	4	838	793
1	5	533	531
2	5	1145	1125
3	5	916	929
4	5	292	286
6	5	1004	973
7	5	1570	1500
10	5	632	590
11	5	1237	1250
12	5	813	805
0	6	2529	2610
1	6	1458	1425
2	6	1068	991
3	6	1285	1319
4	6	818	829
6	6	574	520
7	6	766	719
10	6	1132	1115
12	6	1548	1512
13	6	622	669
17	6	786	729
2	7	1889	1857
3	7	621	543
4	7	416	369
5	7	278	328
7	7	372	369
8	7	421	478
9	7	1063	1035
10	7	2002	1946
11	7	562	659
12	7	393	406
14	7	1167	1202
16	7	554	594
0	8	3272	3287
1	8	1210	1196
2	8	1007	1001
3	8	352	370
4	8	1528	1426
5	8	350	374
6	8	1081	1113
8	8	2440	2477
10	8	1163	1142
11	8	459	497
12	8	2340	2297
13	8	1447	1360
14	8	655	665
15	8	606	667
2	9	3214	3199
3	9	744	636
4	9	1106	1141
5	9	728	748
9	9	2057	2026

Table 18 continued

```
  H   K  FOBS  FCAL       H   K  FOBS  FCAL       H   K  FOBS  FCAL       H   K  FOBS  FCAL       H   K  FOBS  FCAL       H   K  FOBS  FCAL

 **L =  3****              16   2 1041 1086       15   9  535  294       12   6 1157 1132        9   1 1676 1651
  9   9  729  788          18   2 1098 1263       16   9 1044 1030       14   6  695  725       10   1 1742 1811
 10   9 1798 1929          20   2 1132 1106        1  10  769  828       17   6  508  440       13   1  691  808
 11   9  585  618           1   3 1125 1065        3  10  332  247       18   6  647  533       14   1 2200 2108
 14   9 1463 1371           2   3 1926 1867        4  10  951  920        1   7  365  429       15   1 1033 1082
 16   9  521  625           3   3  704  720        5  10  339  350        2   7 2489 2468       16   1 1228 1248
  0  10 2926 2882           4   3  516  484        6  10  852  815        3   7  912  894        0   2  443  390
  1  10  493  515           5   3  396  327        7  10  545  509        4   7  836  914        1   2 2087 2105
  2  10  671  714           6   3  727  773       10  10  701  551        5   7  374  391        3   2 1107 1066
  4  10  913  965           7   3  946 1002       11  10  646  705        6   7  356  230        4   2  860  871
  5  10  586  502           8   3 1208 1241       13  10  597  552        9   7 1197 1144        5   2  545  498
  6  10 1350 1364           9   3  631  691        1  11  447  457       10   7 1521 1550        6   2 1453 1389
  7  10  831  818          10   3  985 1026        3  11  627  663       11   7  585  652        8   2 2686 2582
 10  10 1386 1400          12   3  741  681        4  11  945  930       12   7  744  762        9   2  705  737
 11  10  546  488          13   3  521  605        6  11  602  581       14   7  740  564       10   2  577  634
 12  10 2111 2150          14   3  958  931        8  11  635  683        0   8 3595 3664       11   2 1031 1018
 13  10  898  889          16   3  584  629       11  11  574  517        1   8 2042 2002       12   2 1534 1560
  1  11  440  545           0   4 2393 2290       12  11  546  468        2   8 1478 1396       13   2  698  701
  2  11 1239 1327           1   4 1588 1498        2  12  460  503        3   8 1732 1688       14   2  420  297
  3  11  503  516           4   4  751  676        4  12  791  800        4   8 2305 2305       16   2 1275 1229
  4  11 1116 1114           5   4 1911 1914        6  12 1147 1107        5   8  618  514       18   2 1894 1843
  5  11  500  481           6   4  860  890       11  12  648  475        6   8 1970 1968        1   3 1284 1220
  8  11  529  585           7   4  391  354        4  13 1523 1510        7   8 1231 1115        3   3 1110 1094
 10  11 1269 1328           8   4  682  711        8  13  655  584        8   8 1537 1506        7   3  346  300
 11  11  951  908           9   4  627  489        9  13  598  395        9   8  367  262        8   3  509  613
 14  11  972  988          10   4 1335 1314        0  14  476  420       10   8  747  669        9   3 1017 1016
  0  12  906  927          11   4 1000  971        1  14  504  329       11   8  867  974       10   3 1593 1535
  1  12  864  772          12   4 2128 2138        2  14  950  946       12   8 1556 1533       11   3 1869 1904
  2  12 1037 1049          13   4  557  608        6  14  792  832       13   8  818  753       12   3 1499 1490
  3  12  660  597          14   4  318  169        7  14  666  780        1   9 1196 1107       13   3  610  579
  7  12  622  677          16   4  796  797       **L =  5****           2   9 2971 2667       14   3 1837 1914
  9  12  575  672          18   4  983 1087        1   1  232  294        3   9 1438 1434       15   3  566  639
 10  12  706  690           1   5 1007 1027        2   1 2141 2052        4   9 2808 2909        0   4 1927 2005
 12  12 1765 1838           2   5  516  444        3   1 1445 1363        5   9 1059 1065        1   4  371  354
  2  13 1045 1051           3   5  601  599        4   1  675  974        6   9  770  757        2   4  455  390
  3  13  630  708           4   5 2713 2743        5   1 1553 1539        8   9 1450 1457        3   4  437  437
  4  13  878  934           5   5  769  787        6   1 1030 1035        9   9  844  818        4   4 2192 2137
  8  13  805  780           8   5 1619 1787        7   1 1090 1070       10   9 2326 2385        5   4  292  302
 10  13 1283 1332           9   5  319  373        9   1  574  606       11   9  634  747        6   4  297  215
  0  14 2202 2205          10   5 1790 1746       10   1 1179 1156       14   9 1010  956        7   4 1441 1396
  1  14 1541 1491          12   5  445  444       12   1  371  363       15   9  660  716        8   4  676  695
  2  14 1019 1090          13   5  390  394       14   1  480  437        0  10 2056 2073        9   4 1018 1000
  3  14  770  768          14   5 1094 1071       17   1  501  697        1  10 2193 2233       10   4 1606 1564
  4  14  581  613          15   5  855  943        0   2 3016 2999        2  10  550  587       11   4 1154 1152
  6  14 1001 1020          16   5  933  745        1   2  817  750        3  10  654  735       12   4 1238 1290
  2  15 1669 1746           0   6 4077 4072        2   2 6243 6260        4  10 1131 1144       13   4  994 1096
 **L =  4****               1   6 1358 1324        3   2 3064 3080        5  10  514  521       14   4  547  516
  0   0 2847 2757           2   6 1725 1721        4   2 2136 2167        6  10 1825 1829       16   4  931  954
  1   0 1072 1045           4   6  739  713        5   2 1997 1995        8  10 1530 1399       18   4 1338 1341
  3   0  988  981           5   6  264  143        6   2 2109 2119        9  10  819  867        1   5  953  947
  4   0 2796 2575           6   6  875  883        7   2  275  295       10  10 1020  876        2   5 2297 2198
  5   0  591  576           7   6 1070 1040        8   2  584  574       12  10 1510 1541        3   5 1277 1314
  6   0 2346 2447           8   6  297  272       10   2  680  615        2  11 1690 1700        4   5  705  661
  7   0  521  571           9   6  816  836       11   2  836  915        3  11  491  392        5   5  961  937
  8   0 2279 2145          10   6 1079 1129       12   2 1359 1380        4  11 1165 1156        6   5  392  377
  9   0  544  507          11   6 1071 1067       13   2  820  865        6  11  557  565        7   5  438  401
 10   0  681  678          12   6 1985 2104       15   2  647  653        7  11  565  385        8   5  299  237
 11   0 2571 2582          13   6  505  563        1   3 1082 1063        8  11  932  885       10   5 1575 1521
 12   0 3443 3557          14   6  954  990        2   3 1368 1341        9  11  953  920       11   5  903  898
 13   0 1117 1096          15   6  527  571        3   3 1994 1985       10  11 1501 1506       12   5  412  402
 14   0 1303 1349          16   6  613  526        4   3 1334 1292        0  12 1834 1832       14   5 1932 1969
 15   0  579  573          18   6 1155 1093        5   3  426  412        1  12 1450 1360       15   5  654  628
 16   0 1094 1075           1   7  382  353        6   3 1975 1915        4  12  671  671       16   5  761  777
 17   0  866  928           2   7 1871 1855        7   3  527  508        6  12 1039  993        0   6 2031 1974
 18   0 1743 1784           4   7 2608 2578        8   3 1468 1509        8  12 1006 1044        1   6  706  773
 20   0 1173 1282           6   7  423  257        9   3  457  515       10  12  627  479        5   6  296  218
  1   1  890  887           7   7 1256 1325       10   3  809  759       11  12  932 1013        6   6 2020 2130
  2   1  383  410           8   7 2901 2902       11   3  752  759        2  13 1623 1734        7   6 1234 1229
  3   1  798  706          11   7 1438 1503       13   3  377  411        4  13  959  912        8   6  348  247
  4   1 3134 3047          13   7  546  425       14   3  605  620        8  13 1025 1011       10   6 1622 1636
  5   1  231  174          14   7 1008 1023       15   3  478  389        9  13  824  840       11   6 1354 1348
  6   1 1627 1635          15   7  649  574        0   4 1668 1641        0  14 1754 1749       12   6 2146 2103
  7   1 1235 1240          17   7 1490 1475        1   4 2268 2238        1  14  867  617       13   6 1326 1289
  8   1 3126 3079           0   8 2871 2829        3   4  374  380        2  14  977  883       15   6 1171 1157
  9   1 1464 1462           1   8  514  410        4   4  380  343        6  14 1160 1174       16   6  831 1040
 10   1 2146 2188           2   8 1241 1184        5   4  299  332       **L =  6****            1   7 1558 1545
 11   1  318  275           4   8  352  469        6   4  334  294        0   0 2392 2336        2   7 1967 1865
 12   1  707  713           5   8  625  566        7   4 1089 1028        1   0 2641 2622        4   7  974 1034
 13   1  774  813           6   8  624  676        8   4  572  596        2   0 1367 1325        5   7  652  667
 14   1 2147 2304           8   8  433  457        9   4  554  536        3   0  287  227        8   7 1067 1021
 15   1  438  467          10   8 1162 1165       10   4  410  273        4   0  878  820        9   7  763  707
 16   1 1760 1679          13   8  459  459       13   4 1222 1364        5   0 2139 2124       10   7 1593 1557
 19   1  941 1026          14   8  805  821       14   4  725  757        6   0 3848 3992       14   7 1824 1709
 20   1 1798 1862          17   8  563  545       17   4  742  690        7   0 1527 1559       15   7  717  760
  0   2 3925 3849                                  1   5 1114 1037        8   0 3028 3035       16   7 1395 1395
  1   2 2932 2958                                  3   5 1852 1830        9   0  508  511        0   8  720  704
  2   2  789  820                                  4   5  666  656       10   0  847  758        1   8 1366 1398
  3   2  650  672                                  5   5  958  859       11   0 1474 1447        2   8  910  943
  4   2 2114 2100                                  7   5  521  441       12   0 1442 1476        3   8  628  605
  5   2  596  629                                  9   5  512  484       13   0  813  833        4   8 1177 1220
  6   2 1823 1800                                 10   5  910  865       14   0  817  384        5   8  416  363
  7   2  678  675                                 12   5  585  569       16   0 1235 1234        6   8 2388 2294
  8   2 1781 1853                                 15   5  628  535        1   1 3655 3576        7   8 1040 1026
  9   2 1323 1305                                  0   6 2239 2269        2   1 5200 5153        8   8  879  812
 10   2 1341 1321                                  1   6 1163 1194        3   1 1258 1225       10   8 1106 1143
 11   2 1159 1127                                  4   6 1238 1211        4   1  970 1048       11   8  753  706
 12   2 2647 2626                                  6   6  890  845        5   1  561  464       12   8 1008  900
 14   2  508  496                                  8   6 1669 1875        7   1 1492 1470       13   8  682  557
 15   2  505  602                                 10   6  903  939        8   1 1812 1764       16   8  762  784
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Table 18 continued

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 6				9	6	478	421	9	1	1653	1654	3	8	325	268	11	6	563	468
2	9	612	607	11	6	571	567	10	1	1175	1162	4	8	739	776	14	6	681	695
3	9	501	380	12	6	583	553	11	1	795	829	5	8	1215	1241	15	6	762	831
4	9	740	729	13	6	467	236	12	1	986	987	6	8	1494	1471	1	7	640	593
5	9	353	256	14	6	821	661	13	1	540	515	7	8	1021	925	2	7	1354	1410
6	9	788	820	1	7	286	237	14	1	1894	1798	8	8	626	649	3	7	1796	1769
8	9	1190	1161	2	7	1550	1528	15	1	1102	1038	9	8	636	677	4	7	404	391
9	9	464	591	3	7	983	968	16	1	645	684	10	8	514	521	5	7	477	519
12	9	518	541	5	7	811	761	17	1	774	672	11	8	568	454	6	7	873	901
14	9	640	687	6	7	449	398	18	1	633	612	12	8	1246	1255	7	7	595	564
15	9	501	442	7	7	1174	1162	0	2	1341	1261	13	8	613	609	8	7	397	311
0	10	514	549	8	7	1115	1028	1	2	2167	2143	14	8	616	639	9	7	780	781
1	10	302	218	9	7	1383	1310	2	2	688	650	2	9	296	131	10	7	1832	1749
2	10	347	380	10	7	1325	1374	3	2	2217	2236	3	9	1431	1390	13	7	989	908
3	10	322	208	12	7	695	780	4	2	342	124	4	9	756	773	15	7	766	740
4	10	696	645	13	7	673	628	5	2	633	570	5	9	702	734	0	8	1285	1313
5	10	418	376	16	7	596	601	7	2	1100	1130	8	9	692	714	1	8	1206	1116
6	10	529	469	0	8	1655	1749	8	2	1522	1447	9	9	536	532	4	8	877	902
8	10	822	734	1	8	1652	1679	9	2	706	705	14	9	764	687	5	8	738	720
10	10	644	524	2	8	473	387	10	2	519	400	1	10	925	959	6	8	633	725
11	10	598	555	3	8	764	803	11	2	887	934	2	10	433	427	7	8	792	876
13	10	533	450	4	8	1323	1241	12	2	1080	1027	3	10	526	387	8	8	1671	1673
3	11	825	386	5	8	770	687	13	2	1213	1267	5	10	540	678	9	8	484	483
6	11	652	676	6	8	2238	2182	15	2	250	375	6	10	452	571	11	8	1482	1536
8	11	793	764	7	8	462	464	16	2	857	850	7	10	771	761	12	8	875	921
9	11	630	483	8	8	1805	1840	19	2	1142	1232	11	10	655	566	13	8	646	760
2	12	581	564	9	8	761	820	1	3	618	543	5	11	713	631	1	9	1109	1102
5	12	665	635	11	8	1206	1113	2	3	2211	2150	12	11	1263	1274	2	9	1517	1450
6	12	817	808	12	8	855	831	3	3	1003	998	2	12	836	909	3	9	1133	1167
7	12	777	542	13	8	772	879	5	3	1682	1692	3	12	679	651	4	9	688	665
8	12	524	422	1	9	790	778	6	3	278	278	5	12	481	563	6	9	567	742
4	13	653	700	2	9	2342	2410	8	3	1370	1383	6	12	615	465	8	9	817	747
6	13	1152	1190	3	9	1353	1383	9	3	1717	1659	7	12	505	599	9	9	1006	959
7	13	800	791	4	9	1539	1524	10	3	1033	1050	3	13	868	928	10	9	1524	1570
8	13	961	975	5	9	488	562	11	3	1549	1604	6	13	1082	1140	13	9	1207	1258
1	14	629	551	6	9	701	730	12	3	673	666	6	13	517	553	0	10	1879	1904
2	14	879	932	7	9	458	457	14	3	1433	1373	**L = 9**				1	10	1168	1114
5	14	1120	1124	8	9	1455	1425	15	3	501	508	1	1	326	339	3	10	921	878
L = 7				9	9	1434	1438	16	3	780	770	2	1	1085	1069	4	10	665	842
1	1	954	1007	10	9	2179	2173	17	3	684	732	3	1	770	788	5	10	688	698
2	1	225	301	13	9	851	895	0	4	809	807	4	1	1702	1622	6	10	1346	1318
3	1	765	742	14	9	704	671	1	4	2127	2112	5	1	1198	1223	8	10	889	830
4	1	1056	1085	0	10	1202	1329	2	4	1971	1869	6	1	643	598	9	10	625	584
5	1	230	213	1	10	1310	1252	4	4	1498	1511	7	1	464	388	11	10	1421	1412
6	1	348	418	2	10	541	538	5	4	265	130	8	1	449	449	12	10	575	481
7	1	737	737	3	10	458	487	6	4	1028	1008	10	1	551	489	1	11	729	717
9	1	1294	1293	4	10	1316	1334	7	4	1013	982	11	1	555	497	2	11	759	757
10	1	529	538	6	10	1705	1725	8	4	1627	1540	12	1	316	212	3	11	626	682
11	1	642	604	8	10	1400	1341	9	4	403	386	1	1	541	607	4	11	625	641
14	1	320	163	9	10	734	790	10	4	1187	1161	18	1	594	651	8	11	515	586
16	1	455	485	11	10	2049	1964	11	4	1109	1014	0	2	792	811	9	11	692	752
17	1	542	604	12	10	755	839	12	4	829	807	1	2	1510	1567	10	11	627	671
0	2	1195	1217	13	10	1072	1093	14	4	468	360	2	2	1113	1037	4	12	1145	1090
1	2	2113	2153	1	11	870	805	15	4	707	763	4	2	639	703	5	12	584	545
2	2	1086	1124	2	11	1569	1659	16	4	1072	1109	5	2	489	486	6	12	1093	1175
5	2	1628	1692	3	11	1030	901	18	4	1187	1089	7	2	624	631	2	13	866	915
6	2	1791	1706	4	11	1169	1256	1	5	627	634	8	2	852	839	3	13	914	841
7	2	373	437	7	11	532	529	2	5	1010	1061	2	2	450	426	4	13	1080	1162
8	2	1209	1248	8	11	702	689	3	5	1000	1032	12	2	1204	1248	**L = 10**			
9	2	1084	1006	9	11	675	626	5	5	1418	1286	18	2	511	583	0	0	1006	988
10	2	546	626	10	11	1018	1015	6	5	815	770	1	3	272	285	1	0	1625	1644
12	2	1064	1089	0	12	1222	1187	8	5	1599	1483	3	3	286	174	2	0	686	693
1	3	502	544	1	12	1233	1146	9	5	1418	1330	4	3	1300	1325	3	0	320	318
2	3	1254	1184	2	12	454	290	10	5	1457	1442	5	3	939	934	4	0	1412	1303
3	3	540	584	4	12	1123	1081	11	5	607	622	7	3	790	662	5	0	719	796
4	3	1621	1564	6	12	1345	1445	14	5	1319	1305	8	3	586	518	6	0	3423	3515
6	3	323	236	8	12	907	956	16	5	886	1037	9	3	907	933	7	0	2938	2945
8	3	379	360	9	12	1011	1002	0	6	2375	2435	10	3	996	999	8	0	2671	2634
9	3	685	625	1	13	493	531	1	6	960	1005	11	3	571	506	9	0	1462	1533
10	3	887	893	2	13	1371	1401	2	6	788	723	12	3	485	545	10	0	804	784
13	3	479	348	3	13	475	333	4	6	2390	2348	13	3	518	597	11	0	1852	1962
14	3	881	891	4	13	1590	1587	5	6	757	781	14	3	1029	1085	12	0	1363	1319
18	3	664	572	7	13	666	723	6	6	2181	2031	0	4	707	759	13	0	1894	1805
0	4	2133	2116	0	14	1073	1145	7	6	1792	1818	1	4	933	859	15	0	664	775
1	4	239	238	1	14	529	456	8	6	896	899	2	4	308	363	1	1	2104	2069
2	4	1285	1224	2	14	613	609	9	6	915	839	3	4	415	275	2	1	3159	3223
3	4	251	208	**L = 8**				10	6	711	780	4	4	400	364	3	1	2114	2142
4	4	1012	1005	0	0	3682	3701	11	6	767	752	5	4	437	442	4	1	1445	1315
7	4	548	596	1	0	2000	2031	12	6	1802	1847	6	4	680	685	5	1	1431	1476
8	4	1041	942	2	0	1587	1550	13	6	1302	1297	8	4	1207	1134	6	1	581	641
10	4	300	232	3	0	884	813	15	6	617	562	9	4	453	448	8	1	1715	1713
12	4	712	640	4	0	2355	2339	16	6	959	1010	11	4	393	368	9	1	2207	2252
14	4	683	558	5	0	2865	2882	1	7	530	573	12	4	814	739	10	1	1597	1574
17	4	495	436	6	0	1374	1335	2	7	1240	1251	14	4	466	468	11	1	1605	1681
1	5	367	343	7	0	1771	1776	3	7	1375	1395	1	5	266	325	13	1	775	846
2	5	776	739	8	0	1824	1754	4	7	1894	1842	2	5	939	927	14	1	1001	961
3	5	461	531	9	0	1568	1615	5	7	1065	1101	4	5	1080	1046	15	1	1236	1281
4	5	324	250	11	0	1049	1101	6	7	755	725	7	5	867	892	17	1	944	914
5	5	602	510	12	0	2700	2756	7	7	1255	1201	8	5	422	379	2	2	1394	1294
10	5	662	654	13	0	1796	1865	8	7	737	779	9	5	903	924	1	2	1291	1313
11	5	610	534	16	0	1554	1479	1	8	1256	1239	12	5	530	516	2	2	412	452
12	5	611	796	18	0	1654	1578	2	8	548	387	13	5	617	502	3	2	646	667
13	5	727	811	1	1	1321	1360					0	6	910	866	4	2	1538	1465
14	5	622	592	2	1	2347	2343					2	6	1340	1199	5	2	920	849
0	6	2461	2267	3	1	2911	2848					3	6	660	605	6	2	1194	1068
2	6	851	882	4	1	1650	1547					6	6	1367	1304	7	2	1761	1746
5	6	532	491	5	1	2341	2365					5	6	562	457	8	2	1495	1513
6	6	930	1008	7	1	853	872					6	6	730	676	9	2	316	173
8	6	1763	1696	8	1	1522	1553					6	6	1104	1242	11	2	847	793

Table 18 continued

Column 1

H	K	FOBS	FCAL
L = 10			
12	2	810	776
13	2	841	834
15	2	701	709
1	3	1636	1620
2	3	1782	1795
3	3	1839	1900
4	3	1342	1312
5	3	1731	1678
8	3	1157	1053
9	3	1375	1380
10	3	1455	1443
11	3	571	610
12	3	715	744
13	3	441	372
14	3	1097	1020
15	3	847	811
16	3	492	420
0	4	1656	1632
1	4	1129	1166
2	4	267	254
4	4	1443	1537
5	4	1056	1096
6	4	1849	1805
7	4	1586	1633
8	4	1178	1136
12	4	706	656
13	4	750	698
16	4	532	501
1	5	1005	884
2	5	1525	1548
3	5	1290	1223
4	5	1579	1497
5	5	899	929
6	5	709	664
8	5	709	799
9	5	1045	1145
10	5	672	622
11	5	603	705
14	5	855	820
15	5	652	611
0	6	1773	1694
1	6	1722	1780
2	6	925	911
3	6	620	544
4	6	1317	1333
5	6	1928	1912
6	6	3188	3150
7	6	1913	1956
8	6	1716	1759
9	6	1051	1055
10	6	634	604
11	6	726	657
12	6	751	730
13	6	733	608
1	7	965	1050
2	7	2449	2361
3	7	2264	2266
4	7	1814	1785
5	7	345	276
6	7	419	463
7	7	620	582
8	7	1267	1324
9	7	1555	1421
10	7	1572	1700
11	7	1231	1213
14	7	687	669
0	8	2182	2101
1	8	1098	1117
2	8	429	521
3	8	448	406
5	8	1306	1269
6	8	1153	1259
7	8	1750	1722
8	8	958	984
9	8	550	582
13	8	490	343
2	9	493	510
3	9	1080	1118
8	9	615	566
9	9	739	650
10	9	760	842
11	9	848	869
0	10	420	463
1	10	1058	1107
5	10	1269	1396
6	10	475	606
7	10	588	529
2	11	571	444
3	11	825	773
4	11	656	555
7	11	639	620
0	12	916	939
1	12	835	903
2	12	739	775
3	12	718	777
5	12	880	969
L = 11			
4	1	120	183

Column 2

H	K	FOBS	FCAL
2	1	709	674
3	1	1105	1049
4	1	382	467
6	1	1095	1125
7	1	790	830
9	1	327	343
10	1	1021	1084
11	1	486	439
13	1	708	649
0	2	545	561
1	2	1165	1153
4	2	1422	1326
5	2	1924	1930
6	2	578	610
8	2	1232	1180
9	2	603	601
12	2	885	856
1	3	274	247
2	3	986	967
3	3	445	430
6	3	1261	1293
7	3	488	447
8	3	414	303
9	3	432	468
10	3	745	762
11	3	786	710
13	3	837	786
14	3	722	609
1	4	270	285
2	4	1134	1130
3	4	398	429
4	4	1164	1106
5	4	741	743
6	4	702	737
7	4	455	461
13	4	523	455
14	4	514	416
15	4	550	640
1	5	1185	1119
2	5	341	337
3	5	342	375
4	5	431	433
5	5	304	286
6	5	362	374
9	5	690	646
10	5	573	549
11	5	507	355
14	5	779	736
15	5	569	583
2	6	662	679
3	6	518	532
4	6	291	376
6	6	346	370
9	6	586	409
11	6	836	851
14	6	585	564
1	7	425	505
2	7	718	793
3	7	1153	1217
5	7	410	446
7	7	1087	1067
10	7	1110	1088
13	7	1025	994
0	8	648	628
1	8	756	710
3	8	572	509
4	8	756	799
5	8	1294	1255
7	8	909	879
8	8	1051	1024
9	8	696	747
10	8	1053	1138
12	8	862	913
13	8	652	655
1	9	690	670
2	9	1193	1199
3	9	1400	1457
9	9	1202	1227
10	9	662	714
11	9	558	529
0	10	603	744
1	10	495	520
2	10	586	521
3	10	834	861
5	10	1076	1100
6	10	508	609
7	10	1427	1416
8	10	879	935
1	11	677	583
2	11	447	502
3	11	601	650
1	12	532	541
2	12	586	395
3	12	453	442
4	12	505	382
5	12	657	689
L = 12			
0	0	1833	1875
1	0	2264	2361

Column 3

H	K	FOBS	FCAL
2	0	371	256
3	0	1251	1258
4	0	1969	1976
5	0	1840	1826
6	0	1503	1397
7	0	1966	1893
8	0	1666	1717
9	0	511	497
11	0	650	649
12	0	1554	1573
13	0	1267	1256
1	1	1337	1381
2	1	1927	1821
3	1	1770	1793
4	1	926	934
5	1	1233	1159
6	1	1209	1148
7	1	1046	1027
8	1	1160	1176
9	1	1616	1588
10	1	1684	1652
11	1	1157	1096
13	1	1135	1090
14	1	687	620
15	1	1584	1525
16	1	810	756
0	2	1563	1598
1	2	808	787
2	2	558	527
3	2	1038	1020
4	2	659	711
5	2	1319	1245
6	2	1125	1031
7	2	1495	1588
8	2	1699	1776
9	2	688	667
11	2	818	870
12	2	575	561
13	2	571	563
15	2	601	589
1	3	1169	1188
2	3	1364	1384
3	3	1863	1966
4	3	881	897
5	3	342	270
6	3	455	364
7	3	306	267
8	3	945	965
9	3	1519	1494
10	3	1355	1296
13	3	837	988
14	3	655	622
15	3	1042	995
4	4	2227	2237
0	4	667	639
2	4	1277	1213
3	4	1241	1262
4	4	932	848
5	4	1191	1181
6	4	1548	1516
7	4	1289	1252
8	4	878	921
9	4	439	396
11	4	982	908
12	4	583	509
15	4	672	732
1	5	1418	1452
2	5	1763	1745
3	5	1469	1450
4	5	1666	1659
5	5	311	393
6	5	765	837
9	5	1341	1261
10	5	590	551
11	5	624	588
14	5	576	647
0	6	1676	1650
1	6	1561	1552
4	6	527	403
6	6	1201	1055
8	6	1914	1940
6	6	1335	1507
6	6	1478	1418
6	6	902	885
6	6	569	511
11	6	1049	1072
6	6	1303	1303
13	6	1123	1076
1	7	469	440
2	7	1724	1671
5	7	1585	1552
7	7	1656	1615
4	7	879	874
6	7	664	579
7	7	754	748
8	7	1166	1245
9	7	1410	1360
10	7	1435	1415

Column 4

H	K	FOBS	FCAL
11	7	712	770
13	7	667	555
0	8	1206	1206
1	8	1194	1044
4	8	752	908
5	8	1359	1412
6	8	1039	1028
7	8	1181	1198
8	8	891	856
11	8	861	798
2	9	935	890
3	9	694	864
4	9	815	888
7	9	603	523
9	9	561	678
0	10	528	589
1	10	497	471
2	10	540	505
6	10	822	883
4	11	723	726
6	11	540	407
0	12	441	314
L = 13			
1	1	800	756
4	1	306	339
5	1	577	547
6	1	362	401
7	1	383	419
9	1	597	613
10	1	451	502
15	1	649	653
0	2	1372	1376
1	2	279	273
2	2	612	563
3	2	615	509
5	2	356	394
7	2	1472	1499
10	2	531	526
11	2	583	430
12	2	526	487
1	3	961	1034
2	3	1067	1063
3	3	490	573
4	3	285	317
5	3	655	622
8	3	644	608
9	3	712	676
10	3	402	370
12	3	559	550
1	4	307	240
2	4	700	724
3	4	431	441
4	4	794	752
5	4	894	900
7	4	484	431
9	4	707	718
3	5	305	356
5	5	415	431
9	5	419	369
10	5	573	415
12	5	539	488
13	5	488	400
0	6	536	263
1	6	578	520
2	6	554	518
4	6	553	516
5	6	799	812
7	6	863	909
9	6	1170	1200
11	6	467	236
1	7	620	565
3	7	1417	1263
5	7	450	515
9	7	884	808
10	7	747	656
11	7	793	799
12	7	493	452
0	8	731	705
1	8	908	817
2	8	825	406
5	8	1138	1020
7	8	1468	1459
9	8	919	1091
10	8	953	1008
1	9	758	876
2	9	737	691
3	9	1593	1705
5	9	942	956
9	9	1299	1262
1	10	610	472
5	10	981	1005
7	10	1245	1311
11	10	504	562
3	11	1016	1041
L = 14			
0	0	2341	2231
1	0	1550	1569
2	0	472	447
3	0	846	856

Column 5

H	K	FOBS	FCAL
5	0	2550	2488
6	0	584	567
7	0	2109	2026
8	0	1449	1489
11	0	675	552
12	0	1201	1151
1	1	1056	1068
2	1	1728	1707
3	1	1476	1579
4	1	347	287
6	1	709	741
7	1	1335	1372
9	1	1693	1606
10	1	1488	1447
11	1	516	529
13	1	1345	1346
0	2	2064	2015
1	2	982	1028
2	2	695	726
3	2	809	824
4	2	337	284
5	2	1632	1571
6	2	417	343
7	2	1649	1686
8	2	808	794
11	2	704	616
12	2	632	439
1	3	983	1061
2	3	545	529
3	3	1068	1107
4	3	705	660
7	3	490	595
8	3	491	453
9	3	1206	1259
10	3	849	873
13	3	1126	1085
0	4	855	930
2	4	645	726
3	4	982	1017
5	4	1160	1102
7	4	1212	1193
11	4	923	943
12	4	910	855
13	4	491	318
1	5	1267	1160
2	5	1321	1307
3	5	1727	1702
4	5	808	849
5	5	684	711
7	5	527	480
9	5	1215	1268
10	5	570	511
0	6	1008	985
1	6	642	622
3	6	479	504
5	6	1476	1498
6	6	806	780
7	6	1273	1106
11	6	1629	1580
1	7	674	611
2	7	1320	1453
3	7	1443	1508
4	7	770	739
5	7	505	536
7	7	442	406
8	7	852	789
9	7	917	800
10	7	609	623
0	8	889	787
1	8	992	945
5	8	1168	1113
6	8	925	991
7	8	496	519
8	8	681	685
9	8	578	508
4	9	543	500
L = 15			
2	1	669	535
4	1	381	483
0	2	719	670
1	2	930	923
3	2	420	299
5	2	1211	1132
7	2	733	698
9	2	846	852
1	3	568	558
2	3	1011	1070
3	3	768	756
4	3	497	489
5	3	657	711
6	3	865	730
9	3	770	766
10	3	747	718
0	4	905	892
1	4	452	360
6	4	458	481
7	4	551	545
9	4	499	545
1	5	836	819

Table 18 continued

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 15**				1	0	1430	1399	7	3	897	897	1	2	835	895	4	0	501	492
2	5	665	653	3	0	803	853	9	3	965	911	5	2	800	813	5	0	600	610
3	5	640	539	5	0	1407	1286	10	3	742	682	6	2	491	578	6	0	728	720
0	6	1160	1154	7	0	1709	1768	2	4	480	471	1	3	839	822	7	0	1235	1348
1	6	492	490	10	0	984	1110	3	4	552	503	2	3	419	362	1	1	970	1013
3	6	831	845	11	0	1123	1111	5	4	969	999	3	3	769	698	3	1	1174	1184
5	6	758	830	1	1	979	929	6	4	585	616	9	3	971	1015	4	1	830	693
7	6	731	661	2	1	617	668	7	4	593	709	0	4	627	632	5	1	530	496
9	6	869	808	3	1	1143	1107	3	5	1169	1282	3	4	464	467	1	2	1162	1106
1	7	597	468	6	1	438	452	7	5	951	1016	4	4	449	466	3	2	436	405
2	7	698	642	7	1	677	695	9	5	1232	1361	6	4	478	462	6	2	715	719
3	7	1076	1041	9	1	1890	2010	1	6	924	890	1	5	551	647	7	2	1194	1259
9	7	833	835	10	1	457	459	5	6	1342	1332	2	5	546	545	1	3	873	900
0	8	927	923	0	2	1104	1082	7	6	814	748	3	5	427	385	3	3	991	1036
1	8	514	517	1	2	891	851	1	7	587	630	0	6	972	1030	4	3	465	432
3	8	733	628	3	2	1025	1015	2	7	396	282	3	6	418	444	6	3	464	526
5	8	1273	1270	5	2	1171	1132	3	7	1308	1484	5	6	634	531	1	4	1373	1391
7	8	1298	1349	7	2	1426	1497	5	7	893	860	1	7	533	437	5	4	787	929
1	9	732	785	10	2	768	794	1	8	803	746	2	7	837	858	1	5	815	783
2	9	882	949	11	2	1173	1141	**L = 17****				**L = 18****				3	5	1217	1256
3	9	1681	1721	1	3	717	815	3	1	663	674	0	0	811	688	**L = 19****			
4	9	450	495	3	3	493	533	6	1	580	507	1	0	1634	1730	1	1	608	672
L = 16**				5	3	467	414	0	2	700	714	3	0	396	248	1	2	563	586
0	0	1380	1539																

Table 19

Atomic Coordinates and Isotropic Temperature Factors

Name	x	y	z	B
Rh	0.16618(4)	0.23480(5)	0.23730(4)	2.3*
Cℓ1	0.1727(1)	0.1049(2)	0.2386(1)	3.4*
P1	0.0722(1)	0.2154(2)	0.2424(1)	2.8*
P2	0.1877(1)	0.2637(2)	0.3333(1)	2.4*
P3	0.2531(2)	0.2252(2)	0.1938(1)	2.9*
Cℓ2	0.4111(3)	0.2504(5)	0.4869(4)	17.4*
Cℓ3	0.3976(3)	0.0987(4)	0.4933(3)	14.9*
C1	0.3687(9)	0.179(1)	0.506(1)	12.9*
Cℓ4	0.1302(2)	0.4769(3)	0.0778(3)	13.1*
Cℓ5	0.0451(4)	0.3844(4)	0.0444(3)	18.7*
C2	0.0846(9)	0.410(1)	0.1009(9)	11.2*
O1	0.1447(3)	0.2832(4)	0.1595(3)	3.4
O2	0.1534(3)	0.3341(4)	0.2041(3)	2.9

* These values are equivalent isotropic temperature factors
corresponding to the anisotropic temperature factors shown
in table 20

(Table continued)

Table 19 continued

(a)   Phenyl Carbon Rigid Bodies

Name	x	y	z	B
C111	0.0411(7)	0.1660(5)	0.3022(5)	3.4(3)
C112	-0.0131(6)	0.1760(5)	0.3152(3)	6.4(4)
C113	-0.0363(6)	0.1386(6)	0.3612(5)	8.0(5)
C114	-0.0052(7)	0.0912(5)	0.3941(5)	6.1(4)
C115	0.0491(6)	0.0812(5)	0.3811(3)	5.6(4)
C116	0.0723(6)	0.1186(6)	0.3352(5)	4.1(4)
D	5.432(5)	$x^{1\ddagger}$	0.0180(3)	
E	0.372(8)	$y^{1\ddagger}$	0.1286(3)	
F	0.85(1)	$z^{1\ddagger}$	0.3482(3)	
C121	0.0546(4)	0.1579(5)	0.1814(3)	2.4(3)
C122	0.0437(4)	0.0840(5)	0.1880(3)	3.8(4)
C123	0.0327(4)	0.0413(4)	0.1398(5)	4.9(4)
C124	0.0326(4)	0.0725(5)	0.0851(3)	4.9(4)
C125	0.0436(4)	0.1464(5)	0.0786(3)	5.3(4)
C126	0.0546(4)	0.1891(4)	0.1267(5)	4.5(4)
D	0.208(5)	x^{1}	0.0436(2)	
E	1.666(5)	y^{1}	0.1152(3)	
F	2.528(6)	z^{1}	0.1332(3)	
C131	0.0302(4)	0.2949(5)	0.2324(3)	3.4(3)
C132	0.0465(3)	0.3625(6)	0.2533(2)	3.4(3)
C133	0.0142(4)	0.4235(4)	0.2448(4)	4.2(4)

(Table continued)

Table 19 continued

Name	x	y	z	B
C134	-0.0345(4)	0.4169(5)	0.2154(3)	5.5(4)
C135	-0.0508(3)	0.3493(6)	0.1945(2)	7.0(5)
C136	-0.0185(4)	0.2883(4)	0.2030(4)	6.4(4)
D	2.956(5)	x^1	-0.0022(3)	
E	2.644(5)	y^1	0.3559(4)	
F	2.183(7)	z^1	0.2239(2)	
C211	0.1364(3)	0.3164(6)	0.3707(3)	2.4(3)
C212	0.1371(3)	0.3921(6)	0.3727(3)	3.6(4)
C213	0.0948(4)	0.4298(3)	0.3985(4)	4.5(4)
C214	0.0518(3)	0.3916(6)	0.4224(3)	4.5(4)
C215	0.0511(3)	0.3158(6)	0.4204(3)	4.6(4)
C216	0.0934(4)	0.2782(3)	0.3945(4)	3.9(4)
D	0.035(5)	x^1	0.0941(2)	
E	0.499(5)	y^1	0.3540(3)	
F	5.764(7)	z^1	0.3965(2)	
C221	0.2445(3)	0.3293(4)	0.3348(3)	2.5(3)
C222	0.2447(4)	0.3828(5)	0.2922(3)	2.6(3)
C223	0.2830(4)	0.4381(4)	0.2937(4)	3.2(3)
C224	0.3211(3)	0.4400(4)	0.3377(3)	3.4(3)
C225	0.3209(4)	0.3866(5)	0.3803(3)	3.4(3)
C226	0.2825(4)	0.3312(4)	0.3788(4)	2.7(3)
D	0.594(5)	x^1	0.2827(2)	
E	2.300(6)	y^1	0.3846(3)	
F	5.206(7)	z^1	0.3363(2)	

Table 19 continued

Name	x	y	z	B
C231	0.2074(4)	0.1967(5)	0.3875(4)	2.2(3)
C232	0.2318(4)	0.1319(5)	0.3706(3)	3.3(3)
C233	0.2492(4)	0.0823(4)	0.4121(5)	5.5(4)
C234	0.2421(4)	0.0976(5)	0.4704(4)	5.3(4)
C235	0.2176(4)	0.1625(5)	0.4872(3)	5.7(4)
C236	0.2003(4)	0.2120(4)	0.4457(5)	3.9(4)
D	2.677(6)	x^1	0.2247(2)	
E	1.545(6)	y^1	0.1472(3)	
F	5.464(7)	z^1	0.4289(3)	
C311	0.2469(7)	0.1793(4)	0.1236(5)	2.7(3)
C312	0.1977(5)	0.1526(5)	0.1039(7)	3.3(3)
C313	0.1949(4)	0.1171(5)	0.0509(4)	4.5(4)
C314	0.2412(7)	0.1084(4)	0.0177(5)	3.9(4)
C315	0.2903(5)	0.1352(5)	0.0375(7)	5.4(4)
C316	0.2931(4)	0.1707(5)	0.0905(4)	4.5(4)
D	1.062(5)	x^1	0.2440(3)	
E	0.38(1)	y^1	0.1439(2)	
F	1.86(1)	z^1	0.0707(2)	
C321	0.3020(4)	0.1683(5)	0.2319(3)	2.5(3)
C322	0.3099(4)	0.0958(6)	0.2164(3)	4.2(4)
C323	0.3463(4)	0.0529(4)	0.2470(4)	5.7(4)
C324	0.3747(4)	0.0825(5)	0.2931(3)	5.5(4)
C325	0.3668(4)	0.1550(6)	0.3086(3)	4.8(4)

Table 19 continued

Name	x	y	z	B
C236	0.3304(4)	0.1979(4)	0.2780(4)	3.9(4)
D	2.861(5)	x^1	0.3383(2)	
E	2.276(5)	y^1	0.1254(3)	
F	5.654(7)	z^1	0.2625(2)	
C331	0.2902(4)	0.3077(4)	0.1720(3)	3.1(3)
C332	0.3452(4)	0.3168(5)	0.1814(3)	4.9(4)
C333	0.3703(4)	0.3814(6)	0.1653(3)	6.1(4)
C334	0.3405(4)	0.4370(4)	0.1399(3)	5.0(4)
C335	0.2855(4)	0.4279(5)	0.1305(3)	4.0(4)
C336	0.2603(3)	0.3632(6)	0.1466(3)	3.0(3)
D	3.536(5)	x^1	0.3153(2)	
E	2.933(5)	y^1	0.3723(3)	
F	1.177(7)	z^1	0.1560(2)	

‡ Coordinates of center of gravity of ring.

(Table continued)

Table 19 continued

(b)   Phenyl Hydrogen Atoms

Name	x	y	z	B
H112	-0.0353	0.2102	0.2915	7.0
H113	-0.0752	0.1460	0.3704	8.8
H114	-0.0219	0.0644	0.4271	6.7
H115	0.0713	0.0471	0.4048	6.2
H116	0.1112	0.1112	0.3259	4.5
D	5.432			
E	0.374			
F	1.890			
H122	0.0437	0.0615	0.2272	4.2
H123	0.0248	-0.0118	0.1444	5.4
H124	0.0247	0.0419	0.0505	5.4
H125	0.0436	0.1689	0.0393	5.8
H126	0.0625	0.2422	0.1221	4.9
D	0.208			
E	0.166			
F	3.576			
H132	0.0815	0.3669	0.2743	3.7
H133	0.0261	0.4719	0.2598	4.6
H134	-0.0576	0.4609	0.2094	6.0
H135	-0.0858	0.3449	0.1734	7.7
H136	-0.0303	0.2399	0.1880	7.0

(Table continued)

Table 19 continued

Name	x	y	z	B
D	2.956			
E	2.644			
F	3.230			
H212	0.1682	0.4194	0.3557	4.0
H213	0.0956	0.4842	0.4000	4.9
H214	0.0215	0.4188	0.4409	4.9
H215	0.0200	0.2886	0.4374	5.0
H216	0.0927	0.2238	0.3931	4.3
D	0.035			
E	0.499			
F	6.811			
H222	0.2172	0.3811	0.2607	2.9
H223	0.2830	0.4763	0.2630	3.5
H224	0.3485	0.4800	0.3385	3.7
H225	0.3483	0.3882	0.4118	3.7
H226	0.2826	0.2930	0.4095	3.0
D	0.594			
E	2.300			
F	6.253			
H232	0.2369	0.1208	0.3288	3.6
H233	0.2667	0.0358	0.4000	6.0
H234	0.2545	0.0622	0.5002	5.8
H235	0.2125	0.1736	0.5290	6.3

Table 19 continued

Name	x	y	z	B
H236	0.1827	0.2587	0.4577	4.3
D	2.677			
E	1.545			
F	6.511			
H312	0.1644	0.1589	0.1276	3.6
H313	0.1597	0.0979	0.0367	4.9
H314	0.2392	0.0829	-0.0202	4.3
H315	0.3236	0.1289	0.0138	5.9
H316	0.3284	0.1899	0.1048	4.9
D	1.062			
E	0.38			
F	2.90			
H322	0.2894	0.0745	0.1833	4.6
H323	0.3520	0.0009	0.2359	6.3
H324	0.4008	0.0518	0.3150	6.0
H325	0.3872	0.1763	0.3417	5.3
H326	0.3247	0.2499	0.2891	4.3
D	2.861			
E	2.276			
F	6.701			
H332	0.3666	0.2769	0.1998	5.4
H333	0.4098	0.3879	0.1721	6.7
H334	0.3586	0.4834	0.1283	5.5

Table 19 continued

Name	x	y	z	B
H335	0.2641	0.4678	0.1121	4.4
H336	0.2208	0.3568	0.1398	3.3
D	3.536			
E	2.933			
F	2.224			

Table 20

Anisotropic Temperature Factors $(\overset{\circ}{A}^2 \times 10^3)$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	34.0(9)	24.8(9)	26.8(9)	0.9(7)	- 2.6(7)	3.0(6)
Cℓ1	51(3)	25(2)	55(2)	4(2)	1(2)	1(2)
P1	41(3)	30(3)	35(3)	2(2)	- 5(2)	2(2)
P2	36(3)	25(3)	30(2)	-2(2)	- 2(2)	5(2)
P3	43(3)	33(3)	33(2)	0(3)	0(2)	4(2)
Cℓ2	144(6)	186(7)	330(10)	36(6)	6(6)	4(7)
Cℓ3	182(7)	185(8)	198(7)	37(6)	40(5)	-43(5)
C1	140(20)	38(15)	312(30)	-7(16)	100(20)	-72(17)
Cℓ4	142(6)	115(6)	242(7)	20(5)	33(5)	14(5)
Cℓ5	327(11)	213(8)	172(6)	-54(7)	-119(7)	47(6)
C2	165(21)	123(19)	140(18)	-87(17)	- 66(16)	87(14)

Table 21

Selected Interatomic Distance

Atom 1	Atom	Distance (Å)	
Rh	Cℓ1	2.391(3)	2.401(3)*
Rh	P1	2.362(4)	2.365(4)*
Rh	P2	2.357(3)	2.357(3)*
Rh	P3	2.387(4)	2.391(4)*
Rh	O1	2.081(8)	
Rh	O2	2.005(8)	
P1	C111	1.828(7)	
P1	C121	1.819(7)	
P1	C131	1.809(7)	
P2	C211	1.836(7)	
P2	C221	1.836(7)	
P2	C231	1.818(7)	
P3	C311	1.840(7)	
P3	C321	1.829(7)	
P3	C331	1.842(7)	
O1	O2	1.413(9)	
C1	Cℓ2	1.74(2)	
C1	Cℓ3	1.67(2)	
C2	Cℓ4	1.75(2)	
C2	Cℓ5	1.70(2)	

* A riding correction was performed on these bondlengths with atom 2 assumed to ride on atom 1

Table 22

Selected Intramolecular Angles

Atom 1	Atom 2	Atom 3	Angle (°)
O1	Rh	O2	40.4(3)
O1	Rh	P1	90.0(2)
O1	Rh	P2	101.3(2)
O1	Rh	P3	92.8(2)
O1	Rh	Cℓ1	157.4(2)
O2	Rh	P1	81.7(2)
O2	Rh	P2	141.7(2)
O2	Rh	P3	84.1(2)
O2	Rh	Cℓ1	117.0(2)
P1	Rh	P2	102.7(1)
P1	Rh	P3	154.4(1)
P1	Rh	Cℓ1	85.1(1)
P2	Rh	P3	101.6(1)
P2	Rh	Cℓ1	101.3(1)
P3	Rh	Cℓ1	82.5(1)
Rh	P1	C111	122.0(4)
Rh	P1	C121	106.6(3)
Rh	P1	C131	116.2(4)
Rh	P2	C211	113.4(3)
Rh	P2	C221	110.1(3)
Rh	P2	C231	124.2(3)
Rh	P3	C311	109.4(4)

(Table continued)

Table 22 continued

Atom 1	Atom 2	Atom 3	Angle (°)
Rh	P3	C321	115.9(3)
Rh	P3	C331	120.4(4)
O1	O2	Rh	66.9(4)
O2	O1	Rh	72.7(5)
Rh	O1	C2	157(1)
O2	O1	C2	84(1)
O1	C2	Cℓ4	111(1)
O1	C2	Cℓ5	114(1)
O2	C2	Cℓ4	99(1)
O2	C2	Cℓ5	133(1)
Cℓ2	C1	Cℓ3	111(1)
Cℓ4	C2	Cℓ5	109(1)
P1	C111	C114	179.3(7)
P1	C121	C124	177.0(6)
P1	C131	C134	179.2(6)
P2	C211	C214	176.0(6)
P2	C221	C224	174.1(5)
P2	C231	C234	176.6(6)
P3	C311	C314	178.0(7)
P3	C321	C324	178.2(6)
P3	C331	C334	176.5(7)
C222	H222	O2	157.8
C223	H223	Cℓ1	140.5

(1/2-x, 1/2+y, z)

Table 23

Selected Intramolecular Non-Bonded Contacts

Atom 1	Atom 2	Distance (Å)
Rh	H312	2.90
Cℓ1	H116	2.54
Cℓ1	H232	2.64
Cℓ1	H312	2.77
O11	H126	2.34
C21	H336	2.37
O2	H336	2.28
O2	H222	2.23
O2	H132	2.49
O2	C2	3.26(2)
O1	C2	3.08(2)
H332	H326	2.37

Table 24

Selected Intermolecular Contacts

Atom 1	Atom 4	Symmetry Operation (on atom 2)	Distance ($\overset{\circ}{A}$)
Cℓ1	H223	1/2-x, 1/2+y-1, z	2.66
H122	H134	$\bar{x}$, 1/2+y-1, 1/2-z	2.39
H122	H133	$\bar{x}$, 1/2+y-1, 1/2-z	2.41
H136	H325	1/2+x-1, y, 1/2-z	2.45
H213	H324	1/2-x, 1/2+y, z	2.33
H225	H315	x, 1/2-y, 1/2+z	2.46

Fig. 8

A General View of $[(O_2)RhCl(P(C_6H_5)_3)_3.2CH_2Cl_2]$
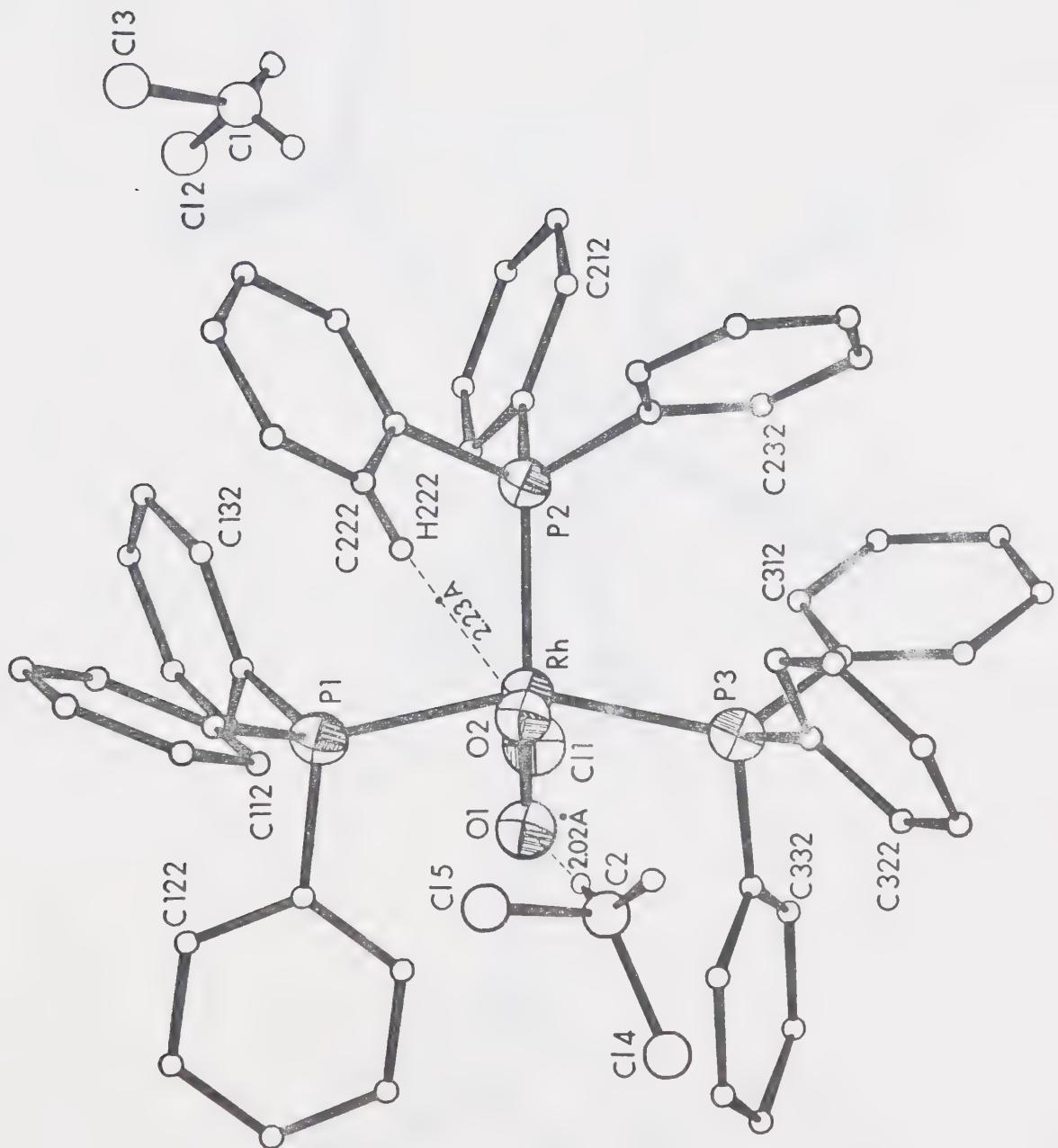
Fig. 9

Equatorial Plane Geometry
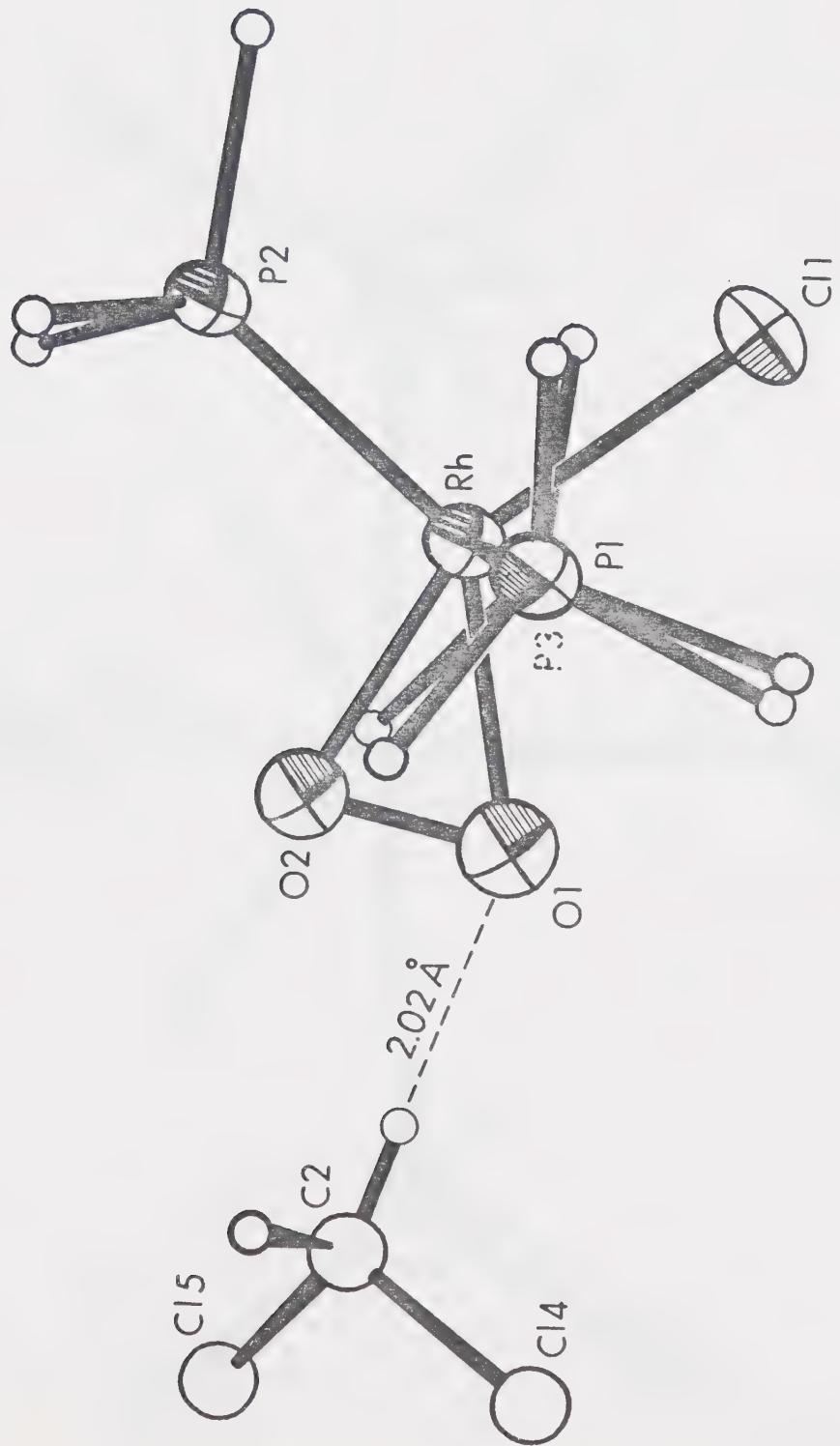
Fig. 10

Central Geometry Viewed down the Rh-P2 Bond
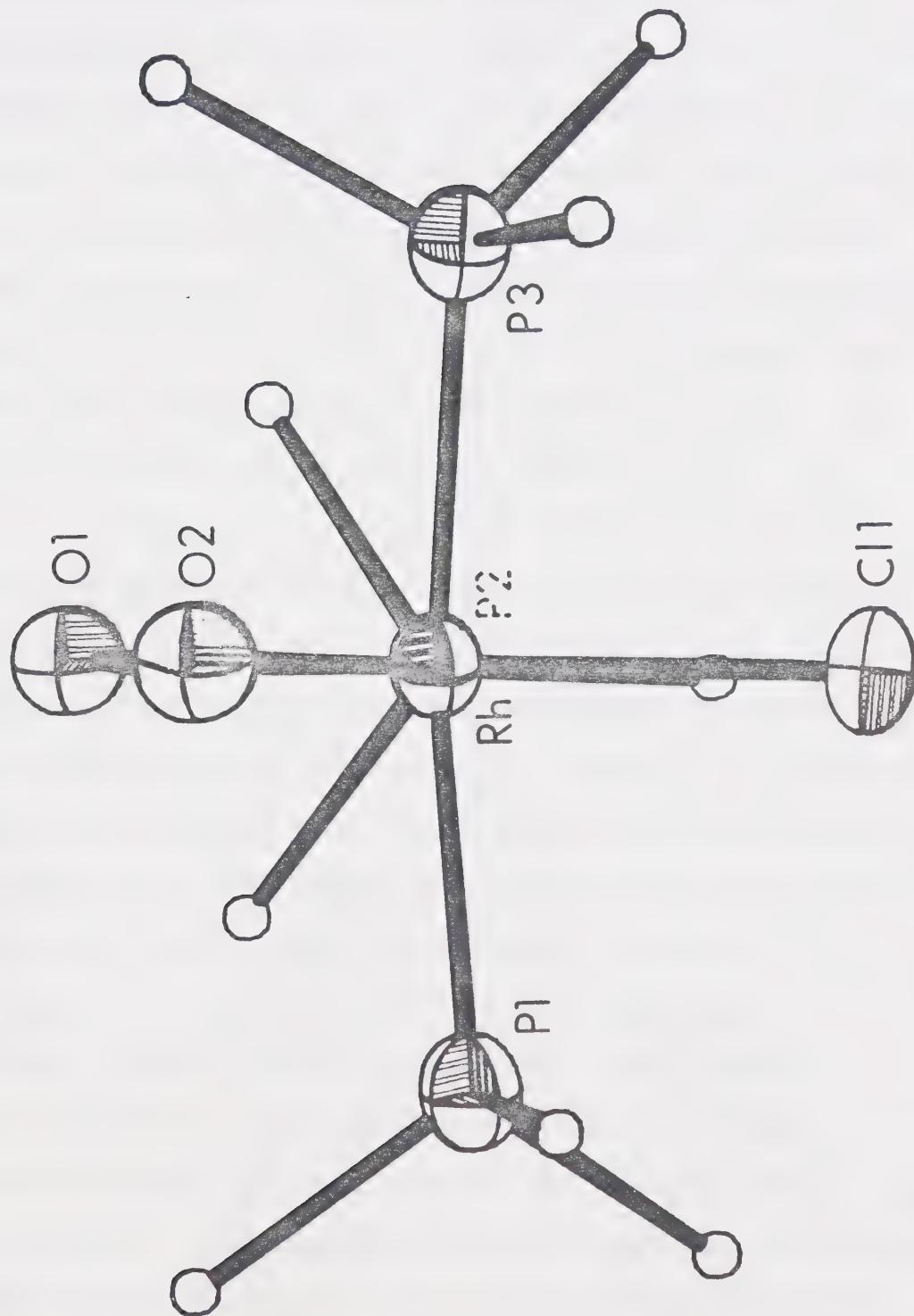
Discussion

The complex has a trigonal bipyramidal structure
if dioxygen is treated as occupying a single coordination
site (which is the preferred view in this thesis).
Alternatively if dioxygen is treated as a bidentate ligand
then the structure is approximately octahedral. In the
trigonal bipyramidal description, the two axial sites
are occupied by triphenylphosphine ligands while the
equatorial sites (Fig. 10) contain the third phosphine
ligand, the chlorine atom (Cℓ1) and the dioxygen molecule
(with both oxygen atoms in the equatorial plane). The
molecule is then coordinatively saturated (Fig. 8).

The rhodium-phosphorus bond lengths (Rh-P1,
2.365(4); Rh-P2, 2.357(3); Rh-P3, 2.391(3) Å) show sig-
nificant variation. The chemically equivalent axial
rhodium-phosphorus (P1 and P3) distances ($\Delta/\sigma \sim 3$) are
interesting, however the actual difference is relatively
small in absolute terms (0.026 Å) and can probably be
ascribed to subtle inter and intramolecular interactions.
Similarly statistically significant variations were ob-
served in the structure of $[(Co(2\text{=phos})_2(O_2)]^+$ [29] and no
chemical significance was assigned. The rhodium-chlorine
bond length of 2.401(3)Å is normal for the rhodium com-
plexes discussed in this thesis (see Chapter VI for further
discussion). The phosphorus-carbon bond lengths average
1.829 Å which is typical for triphenylphosphine comp-

lexes [17,18,129]. The distribution of these distances was consistent with a standard deviation of 0.010 Å (compared with typical values of ~0.007 Å from the least squares refinement) and hence a small systematic error is indicated. No significant variations were observed when the bond lengths were sorted as to phosphine ligand.

The dioxygen ligand is typical of the π-bonded type (classification (1) in the introduction) and the bonding is rationalized in a manner already discussed in Chapter III. Mason[130] has given a slightly different method of viewing such charge transfer as involving a transition similar to $\pi^4 \pi^{*2} \rightarrow \pi^3 \pi^{*3}$. Such a description was only meant to illustrate the effects of transfer of charge from the dioxygen bonding to antibonding orbitals by comparison with dioxygen excited states, and not to illustrate the manner of charge transfer. Parshall [131] considered similar species as involving octahedral coordination with two σ-bonds and no π-bonds being present, however such a description does not correlate the oxygen-oxygen bond length with irreversibility of oxygenation whilst the description of Ibers *et al.*,[18] (derived from Griffith's work) [64,132] does.

The oxygen-oxygen bond length is 1.413(9) Å and is not significantly different from that observed for the dimer, 1.438(9) Å. These distances correspond approximately to that expected for a peroxide [89] and the

complex could be viewed as an octahedral rhodium (III) complex, although as mentioned in the introduction such a classification may be unrealistic. The rhodium-oxygen bond lengths (Rh-O1, 2.081(8); Rh-O2, 2.005(8) Å) appear to be significantly different and hence the ligand is not symmetrically attached. This may reflect differences in the *trans*-ligand (O1 is pseudo-*trans* to P2 and O2 is pseudo-*trans* to Cℓ1). A similar trend is observed in the compound $(O_2)IrCℓ(CO)(P(C_6H_5)_2(C_2H_5))_2$ [20] where the longer metal oxygen distance is pseudo-*trans* to the better π-bonding ligand (in this case carbon monoxide). Detection of this assymmetry in the structures $(O_2)IrX(CO)(P(C_6H_5)_3)_3$, X = Cℓ, I [17,19]; is impossible due to the disorder of X and CO that occurs in these crystals.

There are two other features (both short hydrogen-oxygen contacts) that may contribute to the assymmetry of the rhodium-oxygen distances. The first and probably the most important is the contact of 2.02 Å between one methylene chloride hydrogen atom and O1. This is most clearly seen in Fig. 9. This contact is considerably shorter than the sum of the van der Waals radii (2.5 Å) [120] and it is tempting to describe this interaction as a hydrogen bond [133,138]. The orientation of the methylene chloride molecule is such that the calculated position of the hydrogen atom mentioned is approximately on the line joining C2-O1. This is illustrated

by the near equivalence of the angles: Cl4-C2-O1, 111(1)°; Cl5-C2-O1, 114(1)°, which are in good agreement and expected for such an orientation. The second, somewhat longer, contact (O2-H222, 2.23 Å) is intramolecular and hence it is more difficult to decide whether it is attractive or repulsive in nature, however the hydrogen atom is directed towards the oxygen with the ring having the most bending of any phenyl group in the structure (P2-C221-C224, 174.1(5)°) and very low temperature factors. Thus this interaction could possibly be attractive.

The two dioxygen derivatives described in this thesis both demonstrate that coordinated dioxygen is still basic. In the *bis*-phosphine dimer (Chapter III) the coordinated dioxygen forms a donor bond to another rhodium atom, while in the *tris*-phosphine complex the dioxygen molecule is involved in at least one hydrogen bond.

It is probable that neither of these compounds represent the major dioxygen complex formed in solution by the addition of oxygen to RhCl(P(C$_6$H$_5$)$_3$)$_3$. Rather they result from the conditions of crystallisation. The course of events is likely to be that shown below where triphenylphosphine is represented by P.

$$RhP_3Cl + O_2 \rightleftharpoons RhP_3ClO_2 \qquad\qquad [1]$$

$$RhP_3ClO_2 \rightleftharpoons RhP_2ClO_2 + P \qquad\qquad [2]$$

$$2RhP_2ClO_2 \rightleftharpoons [RhP_2ClO_2]_2 \qquad\qquad [3]$$

$$[RhP_2ClO_2]_2 \rightleftharpoons [RhP_2ClO_2]_2 \, (s) \qquad\qquad [4]$$

$$\text{catalyst}$$

$$P + 1/2 \, O_2 \rightleftharpoons PO \qquad\qquad [5]$$
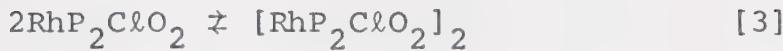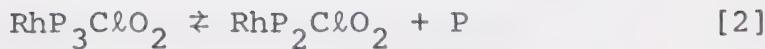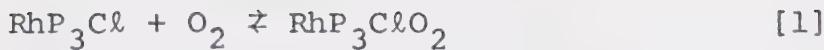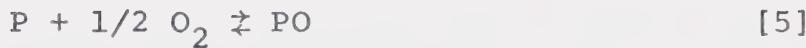
The equilibrium [2] favours RhP_2ClO_2 and only when the phosphine concentration is high does RhP_3ClO_2 form in sufficient quantity to crystallize. The dimer $[RhP_2ClO_2]_2$ has a very low solubility and hence cannot account for the moderately high concentrations of rhodium in solution. It is probable that reaction [3] is extremely slow in view of the steric factors involved in the formation of the dimer. Hence fresh solutions, formed by the addition of dioxygen to RhP_3Cl, correspond to $RhP_2Cl(O_2)$ in agreement with the earlier osmometric studies [3,37], and this species is thermodynamically more stable than $RhP_3Cl(O_2)$ and kinetically stable with respect to its dimer. Reaction [5] is similar to other reactions [43] producing triphenylphosphine oxide and may explain why free triphenylphosphine is only observed in very low concentrations, whilst the oxide is usually observed in solutions having osmometric molecular weights of ~600 [37].

CHAPTER V

The Crystal and Molecular Structures of

the Orange Form of $RhCl(P(C_6H_5)_3)_3$

Experimental

      Orange crystals of $RhCl(P(C_6H_5)_3)_3$ were found to have a "lathe" like habit and were arranged in clusters. A suitable crystal was cut from one of these clusters and after examination under a polarizing microscope, it was mounted on the end of a thin glass fibre so that the needle axis was coincident with the goniometer axis.

      Examination of preliminary Weissenberg and precession photographs indicated that the compound crystallized in the orthorhombic crystal system (Laué symmetry mmm). Absences were found that satisfied the following set of conditions (hkl, no restrictions; 0kl, $k + l = 2n + 1$; h0l, $h = 2n + 1$; hk0, no restrictions). This combination of absences is consistent with the space-groups $Pna2_1$ or $Pnam$.

      The crystal was oriented on a Picker manual diffractometer with the "b" axis coincident with the ϕ axis of the instrument. Several high intensity peaks were scanned for any sign of splitting due to twinning of the crystal (a Laué photograph had been taken earlier as an initial check of the optical examination) and no evidence of twinning was observed.

Lattice parameters were then calculated using diffractometer 2θ values for 13 high angle reflections. The 2θ values were obtained with the independent $\omega/2\theta$ method and utilized the positive and negative 2θ values. The crude lattice parameters from the photographic study were then subjected to a least squares refinement to give the best fit between the observed and calculated 2θ angles. The high angle reflections were chosen so that there was a large variation in the ϕ and χ angles and in all cases the α_1/α_2 splitting was resolved sufficiently to allow the α_1 peak (λ, 1.54051 Å) to be centered. Lattice parameters were a, 19.470(3); b, 12.689(2); c, 18.202(3) Å; $\alpha = \beta = \gamma$, 90°. The density of the compound was measured by flotation in aqueous potassium iodide solution as 1.363 g-cm^{-3}. The density calculated for four molecules in the unit cell is 1.367 g-cm^{-3}.

Intensity data were collected on a Picker manual diffractometer using copper Kα X-radiation, a 2° takeoff angle and a graphite crystal monochromator (002 reflecting plane). The coupled $2\theta/\omega$ method was used with 1 minute scans from $(2\theta-1)°$ to $(2\theta+1)°$, 20 second stationary background counts being taken at the limits of the scan. The diffractometer settings were calculated with the programme MIXG2. Data were only collected to 90° in 2θ because of the rapid decrease in the intensities with increasing 2θ, as observed in the

photographic study. During the data collection eight
standard reflections were measured at eight hour intervals
as an indication of any crystal decomposition (no evidence
of which was found) and all reflections having a count
rate in excess of 10^4 counts-sec^{-1} were noted. A total
of 2212 reflections were measured and of this number 1412
were found to be statistically reliable using the criterion
$I < 3\sigma$ for rejection. After the data collection the high
intensity peaks i.e. those exceeding the linear response
range of the detector, were recollected at lower voltages
and scaled into the data by comparison with less intense
peaks recollected in the same manner. The 0k0 reflections
(at $\chi = 90°$) were measured at 10° intervals in ϕ to
provide experimental confirmation of the correctness of
any absorption correction.

The crystal faces were identified as members
of the forms {1,0,0}, {0,1,0}, {0,0,1} and {1,1,0}.
The dimensions of the crystal as measured under a micro-
scope were ~0.22 x 0.13 x 0.05 mm. Reflection data were
corrected for Lorentz, polarization and absorption effects.
Transmission factors varied from 0.805 to 0.550 (μ(CuKα),
47.6 cm^{-1}). Finally the structure amplitudes and their
standard deviations were calculated using an uncertainty
factor [106] of 0.03.

Structure Solution and Refinement

A three dimensional Patterson map was cal-
culated and carefully examined to resolve the choice of
space group. In this case the structural possibilities
are: (1) $Pna2_1$ with each molecule occupying a general
position and with no constraints on coordinates, (2) Pnam
with each molecule occupying a special position and having
a mirror plane parallel to the "xy" plane. Special
positions involving $\bar{1}$ were not considered a serious option
for this molecule.

These two possibilities give rise to the same
rhodium-rhodium vectors ($1/2 \pm 2x$, $1/2$, $1/2$; $1/2$, $1/2 \pm 2y$,
0; $\pm 2x$, $\pm 2y$, $1/2$) but in principle they should be re-
solvable from vectors involving the lighter heavy atoms
(phosphorus and chlorine). In this structure three of
the heavy ligand atoms have "z" coordinates approximately
equal to that of the rhodium and the fourth atom (later
shown to be the chlorine atom) has a "z" coordinate
definitely different from the "z" coordinate of the rhodium
atom albeit by a relatively small amount (Table 25). Thus
spacegroup $Pna2_1$ is clearly indicated as the correct
spacegroup but the heavy atom fragment ($RhP_3C\ell$) is ap-
proximately planar and perpendicular to the "z" axis.
The "z" coordinate of the rhodium atom was assigned a
value of 0.250 to define the origin of the unit cell in
this direction.

This pseudo mirror plane in the fragment of the molecule used for phasing the structure amplitudes produced a pseudo mirror in the electron density map calculated at this stage i.e. the map represented the electron density of the molecule and superimposed upon this was the electron density of the mirror image although not with equal weight. Solution of the structure was slow and required several electron density difference maps to locate all of the atoms. The second image disappeared as the number of atoms in the model increased. The sequence of events in solving the structure is outlined in Table 26.

Subsequent refinements of the model were routine except for incomplete refinement of the phenyl groups due to an error that was specific to rigid bodies in non-centrosymmetric spacegroups in the least squares refinement programme. Once this error had been detected and corrected the structure converged satisfactorily (Table 27). Structure factors for rhodium, chlorine, phosphorus and carbon were calculated using neutral atom scattering factors derived from Cromer's coefficients [111] and included for rhodium, phosphorus and chlorine the real and imaginary terms for anomalous dispersion. The scattering factors of Mason and Robertson [113] were used for the hydrogen atoms. Throughout the calculations the six carbon atoms of each phenyl group were treated as rigid

bodies of D_{6h} symmetry with carbon-carbon bond lengths
of 1.392 Å. Hydrogen atoms were included at their cal-
culated positions (carbon-hydrogen bond length, 1.0 Å)
with isotropic thermal parameters set at 10% higher than
those of the carbon atoms to which they were attached.
Due to the shortage of data the number of parameters was
a serious concern during the refinement process and the
rigid body model for the phenyl groups enabled the
number of parameters to be minimized. Anisotropic thermal
parameters were introduced for the rhodium, phosphorus
and chlorine atoms only.

At convergence (shift/sigma = 0.12) the standard
deviation of an observation of unit weight was 1.55 which
is certainly acceptable in view of the constraints placed
on the model. A final electron density difference map
showed no systematic residual peaks with the largest
positive and negative peaks being 0.44 and -0.36 e.$Å^{-3}$
respectively (cf. carbon ~3 e.$Å^{-3}$). These peaks were
situated in the vicinity of the 11 and 12 phenyl groups.
The correlation matrix was also printed out in this final
cycle (R_1 = 0.047; R_2 = 0.053) and high correlations were
observed between some carbon temperature factors, however
all coordinate correlations were less than 0.2.

Although the space group Pna2$_1$ contains both
enantiomers the solutions x, y, z and x, y, $\bar{z}$ (or $\bar{x}$, y, z
or x, $\bar{y}$, z) are not equivalent when anomalous scattering

is included in the calculation of the structure factors.
Since the space group is polar the 'incorrect' solution
would have systematic coordinate errors [135] and hence
errors in geometry. For this data set the solution
x, y, $\bar{z}$ can be rejected on the basis of a Hamilton R
factor ratio test [114] with a confidence level of greater
than 99.5%

The atomic coordinates were then entered into
the programme ORFFE II with their respective standard
deviations and the interatomic distances and angles (with
their corresponding standard deviations) calculated.
Rhodium-phosphorus and rhodium-chlorine bond lengths were
also calculated including an allowance for thermal motion.
In this correction the lighter atom (phosphorus or chlorine)
was assumed to ride on the heavier atom (rhodium). This
correction was only appreciable for the rhodium-chlorine
bond length.

Table 25

Assignment of Patterson Peaks

Peak Coordinates			Rel. Height (origin=999)	Assignment	Calc. Height	Calc. Coordinates (from Solution)		
u	v	w						
0.373,	0.504,	0.494	304	$1/2-2x_a, 1/2, 1/2$	198	0.374,	0.500,	0.500
0.500,	0.440,	0.000	295	$1/2, 1/2-2y_a, 0$	198	0.500,	0.442,	0.000
0.125,	0.060,	0.494	158	$2x_a, 2y_a, 1/2$	99	0.126,	0.058,	0.500
0.012,	0.103,	0.456	73	$x_a+x_b, y_a+y_b, 1/2-z_a+z_b$	37	0.012,	0.102,	0.459
0.385,	0.399,	0.050	68	$1/2-x_a+x_b, 1/2-y_a-y_b, z_a-z_b$	37	0.386,	0.398,	0.041
0.116,	0.046,	0.050	66	$x_a-x_b, -y_a+y_b, z_a-z_b$	37	0.114,	0.044,	0.041
0.382,	0.460,	0.456	60	$1/2-x_a+x_b, 1/2+y_a-y_b, 1/2-z_a+z_b$	37	0.386,	0.456,	0.459
0.397,	0.540,	0.494	56	$1/2+2x_b, 1/2, 1/2$	28	0.398,	0.500,	0.500
0.500,	0.354,	0.000	53	$1/2, 1/2-2y_b, 0$	28	0.500,	0.354,	0.000

Assignment Results   a = Rh (0.063, 0.029, 0.250)

b = Cl (-0.051, 0.073, 0.209)

Table 26

Refinement Cycle	Atoms used in Phasing	R_1	New Atoms Located in Corresponding Difference Map
1	Rh, Cℓ	0.425	P1,P2,P3
2	Rh,Cℓ,P1,P2,P3	0.349	$C_{111}-C_{116}$, $C_{131}-C_{136}$, $C_{211}-C_{216}$
3	··	0.304	$C_{321}-C_{326}$, $C_{331}-C_{336}$
4	Rh,Cℓ,P1,P2,P3 $C_{111}-C_{116}$, $C_{131}-C_{136}$ $\Big\{$	0.254	$C_{121}-C_{126}$, $C_{221}-C_{226}$, $\Big\{$
5	$C_{211}-C_{216}$, $C_{321}-C_{326}$, $C_{331}-C_{336}$	0.202	$C_{231}-C_{236}$, $C_{311}-C_{316}$
6	all atoms except	0.139	
7	hydrogen included		

Table 27

Refinement Sequence for $RhCl(P(C_6H_5)_3)_3$

Refinement Cycle	Model	R_1	R_2
7	all atoms isotropic	0.092	0.106
8	anomalous dispersion correction applied	0.090	0.104
9	central atoms anisotropic	0.076	0.088
10	.. .. ..	0.069	0.082
11	hydrogen atoms included	0.065	0.076
12	model x, y, $\bar{z}$ tested	0.081	0.097
13	programme error located	0.051	0.057
14 [a]	.. .. ..	0.047	0.053
15	model x, y, $\bar{z}$ retested	0.052	0.064

a

Test of convergence in cycle 14

Maximum coordinate shift as measured in terms of the corresponding standard deviation 0.05

Maximum thermal parameter shift as measured in terms of the corresponding standard deviation 0.12

Results

Table 28 gives the observed ($|F_o|$) and cal-
culated ($|F_c|$)   structure amplitudes. The atomic
coordinates of all atoms are included in Table 29 with
the anisotropic thermal parameters (U_{ij}) of the central
atoms being listed in Table 30. Other tables include
interatomic distances (Table 31) and interatomic angles
(Table 32) with the inter- and intramolecular non-bonded
contacts listed in Tables 33 and 34 respectively.

Fig. 11 shows the central coordination geometry
viewed perpendicular to the P1-P2-P3 plane. Fig. 12
shows a similar segment of the molecule viewed down the
P1-P3 direction whilst Fig. 13 represents a general view
of the molecule.

Table 28

Observed and Calculated Structure Amplitudes (electrons x 10)

L = 0

H	K	FOBS	FCAL
2	0	1889	1938
4	0	1286	1276
6	0	1613	1567
8	0	2729	2739
10	0	1962	1976
12	0	454	408
14	0	539	542
16	0	651	671
1	1	2358	2409
2	1	392	395
4	1	1915	1891
6	1	989	1004
7	1	1303	1297
9	1	1753	1791
10	1	562	566
13	1	480	491
15	1	411	431
17	1	1008	1017
0	2	480	481
2	2	167	179
3	2	1020	968
4	2	197	246
5	2	1056	1017
6	2	414	410
7	2	778	789
8	2	939	921
9	2	415	491
10	2	632	698
11	2	666	673
13	2	528	499
16	2	631	675
1	3	2081	2039
2	3	253	263
3	3	1113	1157
4	3	939	915
5	3	489	454
7	3	1440	1451
8	3	352	373
9	3	1409	1424
11	3	308	317
12	3	532	506
15	3	368	361
17	3	603	620
0	4	405	451
2	4	1030	1046
4	4	840	846
5	4	499	488
6	4	852	832
7	4	201	229
8	4	1693	1676
10	4	687	665
11	4	449	440
12	4	732	716
13	4	435	454
14	4	292	321
16	4	605	578
1	5	1296	1299
2	5	720	694
4	5	730	763
5	5	378	390
6	5	526	572
7	5	576	656
9	5	795	825
12	5	656	630
13	5	376	391
15	5	427	363
16	5	370	389
1	6	316	274
3	6	1302	1352
4	6	610	608
5	6	1580	1537
9	6	346	382
10	6	327	329
11	6	416	427
12	6	353	307
13	6	307	336
15	6	248	295
1	7	230	210
2	7	543	563
3	7	262	240
4	7	1448	1498
5	7	562	545
6	7	582	602
7	7	459	505
8	7	227	295
10	7	346	345
11	7	378	365
12	7	796	806
14	7	565	518
0	8	373	328
3	8	848	869
5	8	1077	1051
6	8	486	531
7	8	222	206
11	8	579	581
12	8	236	205
2	9	333	314
4	9	1077	1069
6	9	290	273
10	9	311	353
11	9	351	395
0	10	262	231
2	10	908	916
5	10	950	1010
9	10	482	475
0	11	624	580
1	11	542	571
4	11	1317	1295

L = 1

H	K	FOBS	FCAL
2	0	2327	2394
4	0	788	777
6	0	1086	1115
10	0	1474	1444
12	0	635	568
16	0	445	459
0	1	552	566
1	1	1372	1381
3	1	539	531
4	1	441	413
5	1	957	932
6	1	409	441
7	1	721	677
8	1	1025	1005
9	1	1082	1046
10	1	423	444
11	1	1105	1087
12	1	218	193
13	1	234	212
17	1	551	574
1	2	478	469
2	2	482	515
3	2	306	295
4	2	614	605
5	2	1694	1685
6	2	422	449
7	2	1445	1425
8	2	511	501
9	2	195	205
10	2	550	535
11	2	552	529
12	2	644	674
13	2	373	393
14	2	438	458
17	2	374	331
0	3	2067	2039
1	3	1533	1549
2	3	1051	1049
3	3	342	321
4	3	1206	1204
5	3	1136	1116
6	3	1513	1440
7	3	524	517
8	3	567	610
10	3	881	902
11	3	629	641
12	3	478	498
13	3	551	535
15	3	681	679
16	3	554	540
1	4	1099	1106
2	4	1925	1949
3	4	305	330
4	4	670	639
5	4	325	348
6	4	1100	1110
7	4	465	460
8	4	400	338
9	4	731	741
10	4	1331	1356
11	4	900	920
12	4	1110	1086
14	4	427	395
15	4	458	460
16	4	278	346
0	5	1656	1855
1	5	576	553
2	5	1621	1608
3	5	1561	1603
4	5	172	220
5	5	600	599
6	5	762	755
7	5	593	605
8	5	757	739
9	5	437	468
10	5	501	468
11	5	1315	1320
13	5	595	640
14	5	357	394
15	5	628	625
1	6	1456	1503
2	6	512	512
3	6	1105	1129
4	6	345	394
5	6	690	725
6	6	770	746
7	6	1039	1057
9	6	646	671
10	6	376	416
14	6	356	364
15	6	820	764
0	7	494	539
1	7	272	295
2	7	741	796
3	7	643	617
4	7	247	290
5	7	221	251
6	7	844	846
7	7	1075	1082
8	7	637	613
9	7	435	421
10	7	600	560
14	7	790	781
1	8	426	367
2	8	343	377
3	8	702	692
4	8	347	354
5	8	475	526
6	8	375	329
7	8	839	846
8	8	821	843
9	8	546	572
11	8	402	352
2	9	263	289
6	9	811	817
8	9	406	426
9	9	429	361
10	9	549	546
5	10	610	587
6	10	421	407
7	10	649	667
9	10	255	242
0	11	405	350
1	11	253	156
2	11	610	616
3	11	408	435
5	11	356	394

L = 2

H	K	FOBS	FCAL
0	0	4699	5262
2	0	1272	1263
4	0	858	843
6	0	1044	1037
8	0	1670	1699
10	0	989	973
12	0	342	367
14	0	501	521
16	0	816	822
1	1	2331	2370
2	1	530	557
3	1	1295	1284
4	1	2415	2421
6	1	505	529
7	1	1492	1471
8	1	455	454
9	1	1237	1228
10	1	509	493
11	1	504	490
12	1	250	258
13	1	329	340
15	1	541	551
16	1	267	223
17	1	1026	989
0	2	1176	1160
1	2	168	152
2	2	924	907
3	2	2199	2147
4	2	225	217
5	2	658	635
6	2	784	742
7	2	740	715
8	2	1423	1423
9	2	389	350
10	2	924	930
11	2	566	573
12	2	267	257
13	2	414	379
14	2	300	408
15	2	343	316
16	2	893	877
1	3	684	705
2	3	733	747
3	3	1606	1641
5	3	374	400
6	3	546	512
7	3	879	903
8	3	498	482
9	3	1499	1508
10	3	435	479
11	3	342	332
12	3	686	688
14	3	461	497
15	3	470	464
17	3	658	699
0	4	571	588
1	4	534	536
2	4	455	409
3	4	580	574
4	4	254	243
5	4	1092	1101
6	4	731	724
7	4	775	719
8	4	1169	1156
9	4	580	530
10	4	688	684
11	4	275	275
12	4	345	348
13	4	592	549
16	4	484	441
1	5	522	528
2	5	687	711
3	5	413	397
4	5	705	754
5	5	575	542
6	5	472	428
7	5	603	583
9	5	545	547
10	5	322	310
12	5	478	442
13	5	319	374
15	5	315	363
0	6	757	751
1	6	555	537
2	6	219	193
3	6	994	997
5	6	1300	1290
6	6	287	260
8	6	361	352
9	6	386	376
11	6	522	565
12	6	276	313
13	6	353	314
14	6	266	258
1	7	486	483
2	7	626	646
4	7	1126	1121
5	7	546	540
6	7	904	888
7	7	346	302
8	7	267	246
12	7	872	813
14	7	578	608
0	8	628	614
2	8	221	210
3	8	840	890
4	8	255	173
5	8	790	790
6	8	516	524
7	8	297	242
8	8	279	282
10	8	315	212
11	8	733	738
2	9	363	343
3	9	268	250
4	9	885	865
6	9	370	375
10	9	346	415
3	10	852	872
4	10	245	195
5	10	770	758
7	10	271	217
1	11	532	504
2	11	519	548
3	11	256	270
4	11	1142	1093

L = 3

H	K	FOBS	FCAL
2	0	2205	2236
4	0	1935	1965
6	0	1102	1114
8	0	871	827
10	0	1387	1356
12	0	460	439
14	0	294	286
16	0	350	350
0	1	1239	1264
1	1	1288	1299
2	1	708	676
3	1	1750	1661
4	1	1411	1395
5	1	1052	1027
6	1	367	347
7	1	1145	1114
8	1	604	628
9	1	386	381
11	1	905	921
14	1	450	449
17	1	389	430
1	2	1378	1335
2	2	984	930
3	2	1356	1342
4	2	682	669
5	2	854	821
6	2	707	683
7	2	1068	984
8	2	441	425
9	2	1027	1035
10	2	705	721
11	2	541	557
12	2	813	843
13	2	320	280
14	2	576	579
16	2	267	280
17	2	432	367
0	3	1678	1696
1	3	1260	1227
2	3	182	171
3	3	1070	1101
4	3	671	672
5	3	750	717
6	3	888	879
7	3	297	345
8	3	685	683
9	3	674	664
10	3	1040	962
11	3	1028	997
12	3	502	479
13	3	607	602
14	3	307	309
15	3	394	398
16	3	485	453
1	4	1272	1292
2	4	1014	1007
3	4	708	712
4	4	1062	1070
5	4	419	396
6	4	510	483
7	4	390	427
8	4	214	241
9	4	582	548
10	4	905	955
11	4	577	628
12	4	877	875
14	4	330	378
15	4	404	457
16	4	287	250
0	5	1492	1490
1	5	876	861
2	5	1164	1180
3	5	803	814
4	5	341	363
5	5	1256	1307
6	5	906	868
7	5	220	248
8	5	953	927
9	5	513	504
10	5	569	600
11	5	843	866
13	5	475	456
14	5	553	541
15	5	343	311
1	6	1553	1593
2	6	811	824
3	6	872	901
4	6	618	587
5	6	591	567
6	6	772	812
7	6	973	989
9	6	651	659
10	6	432	463
13	6	491	490
14	6	354	386
0	7	1024	1039
1	7	233	220
2	7	1152	1140
3	7	572	539
6	7	845	882
7	7	746	760
8	7	764	748
10	7	397	461
12	7	231	149
13	7	313	316
1	8	506	497
3	8	296	296
6	8	382	379
7	8	724	751
8	8	368	318
9	8	486	509
11	8	622	570
0	9	295	309
2	9	405	367
4	9	221	182

123

Table 28 continued

L = 3***

H	K	FOBS	FCAL
6	9	651	647
7	9	262	248
8	9	492	519
9	9	331	307
10	9	602	626
1	10	420	435
5	10	587	597
6	10	387	348
7	10	946	911
0	11	502	506
1	11	211	115
2	11	510	512
3	11	308	345

L = 4***

H	K	FOBS	FCAL
0	0	1059	1098
2	0	1000	954
6	0	1048	1039
8	0	1422	1467
10	0	707	675
12	0	516	569
14	0	550	479
16	0	803	851
1	1	2148	2121
2	1	743	740
3	1	578	646
4	1	649	667
5	1	294	220
6	1	257	249
7	1	1130	1120
9	1	1215	1206
10	1	661	654
11	1	298	306
12	1	515	520
13	1	626	633
15	1	530	570
16	1	371	354
17	1	861	875
0	2	2391	2361
1	2	403	394
2	2	640	670
3	2	764	766
4	2	242	210
6	2	647	614
7	2	557	517
8	2	1455	1474
9	2	809	820
10	2	992	979
11	2	452	414
13	2	555	612
15	2	416	393
16	2	851	842
1	3	1515	1506
2	3	576	569
3	3	226	232
4	3	736	726
5	3	425	450
6	3	476	485
7	3	674	664
8	3	392	428
9	3	1364	1396
11	3	319	315
12	3	472	439
14	3	719	633
15	3	420	386
0	4	1213	1233
1	4	284	298
2	4	330	305
3	4	451	425
4	4	747	712
5	4	606	636
6	4	617	632
7	4	482	488
8	4	1149	1176
9	4	369	335
10	4	741	727
13	4	688	673
14	4	264	290
16	4	325	367
1	5	559	582
2	5	785	820
3	5	369	374
4	5	1403	1365
5	5	396	405
6	5	644	685
7	5	897	905
9	5	781	768
10	5	433	399
11	5	308	335
12	5	423	455
13	5	405	379
15	5	271	358
0	6	847	843
1	6	500	498
2	6	534	531
3	6	1139	1169
4	6	298	291
5	6	1206	1245
6	6	291	299
8	6	595	590
9	6	315	295
11	6	508	518
13	6	440	449
1	7	438	420
2	7	597	553
3	7	216	239
4	7	825	845
5	7	421	412
6	7	948	906
8	7	304	278
10	7	316	367
11	7	311	258
12	7	736	736
0	8	628	614
1	8	224	146
2	8	221	197
3	8	664	662
4	8	456	451
5	8	763	735
6	8	445	415
10	8	265	309
11	8	816	792
1	9	234	227
2	9	323	320
3	9	226	209
4	9	840	893
6	9	454	505
8	9	265	257
9	9	236	213
10	9	316	315
3	10	794	780
4	10	283	276
5	10	825	827
7	10	361	330
1	11	426	402
2	11	410	455
3	11	316	335

L = 5***

H	K	FOBS	FCAL
2	0	1740	1746
4	0	1710	1703
6	0	1066	1051
8	0	1049	996
10	0	980	972
12	0	268	367
14	0	265	133
0	1	646	621
1	1	889	895
2	1	521	564
3	1	1402	1452
4	1	450	470
5	1	1215	1218
6	1	835	836
7	1	1244	1263
8	1	463	483
9	1	373	368
10	1	231	240
11	1	887	885
13	1	432	477
14	1	372	379
15	1	350	375
1	2	749	768
2	2	609	578
3	2	626	608
4	2	838	760
5	2	837	760
6	2	976	919
7	2	747	686
8	2	458	415
9	2	555	542
10	2	932	912
11	2	407	389
12	2	817	775
14	2	657	643
15	2	264	246
16	2	434	414
0	3	1100	1079
1	3	307	284
2	3	780	758
3	3	589	574
4	3	515	518
6	3	540	581
7	3	397	429
8	3	608	564
9	3	597	559
10	3	550	606
11	3	988	993
12	3	421	381
13	3	535	537
15	3	483	524
1	4	305	468
2	4	951	919
3	4	884	922
4	4	394	439
5	4	198	129
6	4	588	530
7	4	970	935
8	4	211	193
9	4	509	526
10	4	786	829
11	4	502	483
12	4	909	855
14	4	282	313
15	4	605	582
0	5	671	662
1	5	612	623
2	5	1066	1069
3	5	517	533
4	5	353	379
5	5	861	879
6	5	922	927
7	5	263	210
9	5	305	308
10	5	306	319
11	5	867	893
1	6	1159	1176
2	6	963	929
3	6	830	824
4	6	256	289
5	6	537	539
6	6	558	627
7	6	1076	1068
9	6	527	494
10	6	399	332
13	6	436	487
14	6	299	255
0	7	620	625
2	7	839	878
3	7	280	315
4	7	342	341
5	7	676	645
7	7	557	527
8	7	596	608
10	7	399	352
13	7	336	333
1	8	481	458
3	8	294	245
4	8	289	235
5	8	261	296
6	8	316	298
7	8	509	554
8	8	401	431
11	8	588	563
0	9	411	440
1	9	345	336
2	9	435	460
6	9	782	743
8	9	541	536
1	10	421	419
3	10	372	314
5	10	430	416
7	10	890	852
0	11	512	542
2	11	495	488

L = 6***

H	K	FOBS	FCAL
0	0	2578	2629
2	0	999	983
4	0	913	950
6	0	906	884
8	0	1473	1474
10	0	756	739
12	0	889	898
14	0	790	838
16	0	646	599
1	1	1487	1489
2	1	217	197
3	1	537	555
4	1	241	234
5	1	550	596
7	1	767	787
8	1	230	240
9	1	1377	1427
10	1	627	626
11	1	357	318
12	1	414	404
13	1	644	639
15	1	307	393
0	2	1239	1229
1	2	849	817
2	2	929	928
3	2	803	845
4	2	295	333
5	2	957	942
7	2	205	248
8	2	943	918
9	2	647	609
10	2	896	902
11	2	411	406
12	2	255	184
13	2	612	585
15	2	348	391
16	2	611	617
1	3	1064	1051
2	3	336	298
3	3	781	802
4	3	198	202
5	3	305	331
6	3	337	331
7	3	779	799
9	3	782	773
11	3	503	471
12	3	304	396
14	3	541	533
15	3	406	390
0	4	1427	1452
1	4	346	347
2	4	657	713
3	4	262	261
4	4	811	811
5	4	546	558
6	4	721	683
7	4	260	288
8	4	1090	1123
10	4	740	729
11	4	279	304
13	4	503	492
14	4	335	327
15	4	269	276
1	5	999	949
2	5	844	859
4	5	1496	1460
5	5	310	289
6	5	843	795
7	5	1001	992
9	5	1009	1017
12	5	572	558
13	5	344	455
14	5	305	351
0	6	1008	1075
1	6	429	439
2	6	550	575
3	6	1310	1345
5	6	1274	1276
6	6	313	288
8	6	562	495
9	6	426	387
10	6	255	275
11	6	537	526
13	6	628	577
1	7	573	573
2	7	782	764
3	7	390	441
4	7	1156	1212
5	7	482	448
6	7	964	937
7	7	226	212
10	7	387	423
12	7	725	686
0	8	417	353
2	8	283	267
3	8	384	395
4	8	432	424
5	8	603	615
6	8	242	268
11	8	487	512
1	9	353	352
2	9	220	227
4	9	639	636
6	9	461	469
9	9	351	336
1	10	264	308
2	10	301	265
3	10	928	890
5	10	938	914

L = 7***

H	K	FOBS	FCAL
2	0	1832	1852
4	0	1513	1472
6	0	541	516
8	0	671	678
10	0	1081	1116
12	0	842	790
0	1	446	471
1	1	1112	1101
2	1	411	363
3	1	1708	1664
4	1	342	356
5	1	1143	1171
6	1	928	901
8	1	900	905
9	1	432	426
11	1	916	957
12	1	293	278
13	1	521	598
14	1	344	337
1	2	730	700
2	2	1057	1059
3	2	754	773
4	2	971	1044
5	2	806	815
6	2	740	776
7	2	637	678
8	2	358	447
9	2	588	591
10	2	761	760
12	2	676	719
14	2	504	513
15	2	290	252
0	3	814	813
1	3	516	502
2	3	700	667
3	3	305	293
5	3	275	246
6	3	290	294
7	3	364	400
8	3	363	354
9	3	376	486
10	3	387	361
11	3	886	899
12	3	283	233
13	3	427	366
14	3	330	296
15	3	473	472
1	4	238	184
2	4	1022	991
4	4	362	391
5	4	307	245
6	4	545	540
7	4	348	365
9	4	269	379
10	4	916	935
11	4	370	308
12	4	603	575
0	5	862	844
1	5	596	612
2	5	904	874
3	5	1068	1093
5	5	571	578
6	5	524	564
8	5	673	684
9	5	520	494
10	5	372	386
11	5	871	895
14	5	617	596
1	6	1076	1082
2	6	568	560
3	6	437	408
4	6	481	420
5	6	443	480
6	6	497	510
7	6	1034	1023
9	6	560	519
10	6	323	315
12	6	297	252
13	6	545	527
0	7	905	847
2	7	728	720
3	7	226	238
5	7	232	241
6	7	652	643
7	7	236	265
8	7	580	561
9	7	230	210
10	7	523	454
1	8	359	302
4	8	360	339
5	8	374	383
7	8	557	547
8	8	241	224
9	8	356	358
0	9	305	319
1	9	252	251
2	9	300	383
3	9	264	261
6	9	705	732
8	9	523	568
1	10	696	681
3	10	553	534
5	10	359	405

L = 8***

H	K	FOBS	FCAL
0	0	1970	1954
2	0	507	480
4	0	374	385
6	0	686	665
8	0	1067	1062
10	0	395	418
12	0	904	910
14	0	500	525

Table 28 continued

Column 1:

```
H  K FOBS FCAL
 **L =  8*****
 1  1 1316 1309
 2  1  348  320
 3  1  203  197
 4  1  582  549
 5  1  460  476
 7  1  894  952
 8  1  309  316
 9  1  959  987
10  1  454  457
12  1  443  416
13  1  418  424
15  1  455  464
 0  2 1205 1184
 1  2  343  361
 2  2  568  542
 3  2  604  618
 5  2  582  570
 6  2  545  556
 7  2  463  458
 8  2  856  840
 9  2  566  574
10  2  613  595
11  2  329  235
13  2  438  458
14  2  261  230
 1  3  493  500
 2  3  203  160
 3  3  320  264
 4  3  889  873
 5  3  325  368
 6  3  593  590
 7  3  770  728
 9  3  821  797
10  3  245  150
12  3  463  397
14  3  517  502
 0  4  896  861
 2  4  506  513
 3  4  501  466
 4  4  448  487
 5  4  754  744
 6  4  469  503
 7  4  468  429
 8  4 1041 1119
 9  4  255  198
10  4  436  389
13  4  650  653
14  4  301  281
 1  5  894  910
 2  5  445  466
 4  5 1015 1071
 5  5  311  262
 6  5  462  447
 7  5  680  684
 8  5  265  214
 9  5  810  794
10  5  387  391
12  5  720  674
 0  6  842  816
 2  6  564  520
 3  6 1313 1293
 5  6 1197 1153
 8  6  596  559
 9  6  341  351
10  6  413  477
11  6  717  685
 1  7  559  593
 2  7  518  438
 4  7 1071 1032
 5  7  401  405
 6  7  569  618
 9  7  475  431
10  7  281  272
 0  8  470  518
 3  8  384  443
 5  8  566  635
 9  8  243  214
 1  9  330  252
 2  9  314  262
 4  9  652  578
 6  9  412  390
 2 10  289  346
 3 10  579  611
 **L =  9*****
 2  0 1472 1438
 4  0 1401 1432
 6  0 1118 1144
 8  0  428  458
10  0 1019  974
12  0  815  827
14  0  387  439
 0  1  936  979
 1  1  944  920
 3  1 1012 1055
 4  1  356  301
```

Column 2:

```
H  K FOBS FCAL
 5  1  863  868
 6  1  400  442
 7  1  687  707
 8  1  415  384
 9  1  387  394
11  1  678  730
13  1  587  592
 1  2  334  262
 2  2  757  729
 3  2  482  491
 4  2  597  634
 5  2  438  583
 6  2  786  824
 7  2  436  474
 8  2  354  376
10  2  520  532
12  2  543  579
13  2  391  330
14  2  569  497
 0  3  752  807
 1  3  659  642
 3  3  621  622
 5  3  992  973
 7  3  709  722
 9  3  321  300
10  3  326  324
11  3  812  818
13  3  469  463
 1  4  291  258
 2  4  724  755
 3  4  257  234
 4  4  595  525
 5  4  223  240
 6  4  624  595
 7  4  267  262
10  4  824  870
11  4  302  293
12  4  353  362
 0  5  633  633
 2  5  713  703
 3  5  700  676
 5  5  263  572
 6  5  563  595
 7  5  260  263
 9  5  493  465
10  5  395  447
11  5  521  543
 1  6  949  979
 2  6  348  341
 3  6  643  678
 5  6  480  507
 6  6  271  205
 7  6  679  643
 9  6  599  581
11  6  332  291
 0  7  586  561
 2  7  748  738
 5  7  270  214
 6  7  699  698
 7  7  490  534
10  7  447  392
 1  8  345  342
 3  8  305  342
 5  8  322  355
 7  8  601  584
 9  8  493  460
 2  9  607  566
 **L = 10*****
 0  0 1152 1130
 2  0  438  361
 4  0  226  245
 6  0  762  821
 8  0  921  914
10  0  343  399
12  0  649  643
14  0  445  448
 1  1  918  957
 2  1  691  711
 4  1  446  465
 5  1  533  486
 6  1  374  357
 7  1  657  630
 8  1  428  402
 9  1  617  629
10  1  484  502
11  1  381  317
12  1  555  549
13  1  507  518
 0  2  897  919
 3  2  528  541
 5  2  529  507
 6  2  455  511
 8  2  847  872
 9  2  376  403
10  2  324  382
```

Column 3:

```
H  K FOBS FCAL
11  2  382  340
12  2  253  198
13  2  368  372
 1  3  669  711
 2  3  361  389
 3  3  328  311
 4  3  631  645
 5  3  235  180
 6  3  410  377
 7  3  539  591
 9  3  774  751
12  3  497  454
 0  4  707  661
 1  4  302  252
 2  4  437  433
 3  4  568  610
 4  4  399  367
 5  4  756  790
 6  4  357  245
 7  4  414  407
 8  4  787  802
11  4  374  354
 1  5  823  783
 2  5  570  582
 4  5  917  938
 6  5  401  360
 7  5  804  819
 8  5  232  104
 9  5  565  536
10  5  562  589
12  5  753  751
 0  6  746  705
 1  6  400  401
 2  6  419  504
 3  6  990  943
 5  6  812  773
 8  6  388  377
10  6  401  400
 1  7  293  335
 2  7  260  259
 4  7  713  656
 6  7  264  292
 0  8  269  318
 3  8  651  613
 4  8  273  230
 5  8  501  493
 6  8  257  271
 2  9  316  333
 **L = 11*****
 0  0  652    0
 2  0  881  840
 4  0 1090 1162
 6  0  845  859
 8  0  418  427
10  0  795  811
12  0  655  671
 0  1  530  583
 1  1  569  568
 3  1 1017 1046
 4  1  253  241
 5  1  729  728
 6  1  236  228
 7  1  706  700
 8  1  283  349
 9  1  424  411
10  1  272  230
11  1  766  783
13  1  569  550
 2  2  704  680
 4  2  696  642
 5  2  243  287
 6  2  743  738
 7  2  267  256
 8  2  247  230
10  2  424  488
12  2  626  617
13  2  281  266
 0  3  448  454
 1  3  456  491
 3  3  617  590
 5  3  648  682
 7  3  492  473
11  3  575  578
 1  4  301  350
 2  4  712  769
 3  4  306  347
 4  4  682  662
 6  4  444  460
 7  4  297  316
 9  4  321  231
10  4  601  550
 0  5  421  415
 1  5  290  281
 2  5  505  541
 3  5  513  426
```

Column 4:

```
H  K FOBS FCAL
 4  5  273  209
 5  5  435  371
 6  5  541  583
 8  5  374  335
 9  5  273  322
 1  6  731  750
 2  6  321  359
 3  6  586  598
 5  6  579  538
 7  6  610  541
 9  6  439  470
 0  7  473  442
 2  7  631  712
 4  7  247  241
 6  7  583  574
 1  8  565  548
 3  8  410  356
 4  8  332  356
 **L = 12*****
 0  0 1111 1130
 2  0  588  633
 4  0  352  298
 6  0  666  828
 8  0  974  967
10  0  352  369
 1  1  649  635
 2  1  396  420
 4  1  481  516
 5  1  261  289
 7  1  591  576
 9  1  647  637
10  1  407  418
 0  2  632  622
 3  2  484  478
 5  2  505  507
 7  2  286  340
 8  2  588  596
 9  2  365  439
10  2  406  443
11  2  252  200
 1  3  646  677
 2  3  273  348
 3  3  357  415
 4  3  665  668
 6  3  421  403
 7  3  335  370
 8  3  350  370
 9  3  567  620
 0  4  906  900
 2  4  546  609
 3  4  516  545
 4  4  369  395
 5  4  556  574
 7  4  398  449
 8  4  672  654
 9  4  247  117
10  4  383  388
 1  5  768  729
 2  5  293  244
 4  5  936  896
 6  5  490  561
 7  5  568  560
 9  5  635  634
 0  6  457  446
 3  6  686  650
 4  6  241  113
 5  6  765  745
 6  6  276  225
 8  6  303  294
 2  7  422  417
 4  7  588  553
 7  7  373  362
 0  8  332  325
```

Column 5:

```
H  K FOBS FCAL
 **L = 13*****
 2  0 1062 1045
 4  0 1087 1248
 6  0  724  717
 8  0  372  382
10  0  835  901
 0  1  466  478
 1  1  445  389
 2  1  406  418
 3  1  925  954
 5  1  546  513
 6  1  370  353
 7  1  387  452
 8  1  334  327
 9  1  509  507
11  1  715  698
 0  2  294  296
 1  2  652  681
 2  2  494  514
 4  2  399  328
 5  2  279  238
 8  2  301  285
10  2  473  470
```

Column 6:

```
H  K FOBS FCAL
 0  3  368  351
 1  3  493  526
 3  3  385  427
 5  3  301  366
 7  3  506  457
 2  4  764  747
 3  4  297  350
 4  4  518  522
 5  4  262  327
 6  4  454  471
 7  4  270  247
 0  5  312  305
 1  5  443  439
 2  5  479  465
 3  5  548  524
 5  5  330  359
 6  5  512  465
 8  5  384  350
 1  6  525  563
 2  6  272  280
 3  6  360  313
 5  6  451  413
 0  7  520  516
 2  7  486  561
 3  7  279  205
 **L = 14*****
 0  0  899  865
 2  0  610  635
 6  0  673  694
 8  0  831  857
 1  1  652  681
 2  1  331  326
 4  1  457  457
 5  1  497  496
 6  1  239  224
 7  1  411  508
 9  1  695  667
 0  2  525  545
 1  2  263  248
 2  2  396  365
 3  2  369  349
 5  2  329  335
 7  2  331  290
 8  2  453  433
 9  2  237  241
 1  3  587  584
 2  3  334  325
 3  3  391  382
 4  3  469  432
 6  3  283  357
 7  3  313  291
 8  3  248  250
 0  4  823  820
 2  4  630  709
 3  4  504  509
 5  4  302  320
 6  4  405  386
 7  4  309  268
 1  5  633  693
 3  5  244  136
 4  5  657  666
 0  6  283  264
 3  6  645  556
 **L = 15*****
 2  0  596  638
 4  0 1118 1172
 6  0  426  448
 0  1  354  380
 1  1  233  145
 2  1  253  345
 3  1  647  688
 5  1  602  628
 6  1  245  337
 7  1  326  342
 1  2  326  378
 2  2  289  275
 4  2  311  335
 6  2  266  243
 7  2  265  243
 3  3  357  336
 5  3  354  393
 2  4  421  377
 3  4  272  268
 4  4  513  498
 0  5  374  271
 1  5  288  323
 **L = 16*****
 0  0  598  617
 2  0  230  219
 1  1  563  571
 4  1  246  207
 0  2  547  610
 2  2  295  224
 3  2  395  428
 1  3  384  365
```

Table 29

Atomic Coordinates and Isotropic Temperature Factors

for the Unique Contents of the Unit Cell

Name	x	y	z	B *
Rh	0.06304(5)	0.02892(9)	0.2500(0)	2.38
Cℓ	-0.0508(2)	0.0726(3)	0.2088(3)	3.88
P1	0.0800(2)	0.2085(3)	0.2555(4)	2.91
P2	0.1723(2)	-0.0199(3)	0.2607(4)	2.81
P3	0.0154(2)	-0.1362(3)	0.2757(2)	2.71

* These values are equivalent isotropic temperature
factors corresponding to the anisotropic temperature
factors given in table 30

Table 29 continued

(a) Phenyl Carbon Rigid Bodies

Name	x	y	z	B
C111	0.0247(6)	0.273(1)	0.3240(6)	3.0(4)
C112	0.0372(5)	0.377(1)	0.3439(5)	7.6(7)
C113	-0.0054(7)	0.4268(7)	0.3945(8)	8.4(7)
C114	-0.0605(6)	0.373(1)	0.4253(6)	5.8(5)
C115	-0.0730(5)	0.268(1)	0.4054(5)	4.8(4)
C116	-0.0305(7)	0.2184(7)	0.3548(8)	4.0(4)
D	0.318(8)	$x^{1\ddagger}$	-0.0179(4)	
E	0.669(8)	$y^{1\ddagger}$	0.3226(7)	
F	5.783(9)	$z^{1\ddagger}$	0.3746(4)	
C121	0.0606(6)	0.278(1)	0.1699(6)	3.4(4)
C122	0.0657(6)	0.2186(7)	0.1059(8)	3.9(4)
C123	0.0549(7)	0.266(1)	0.0379(6)	6.2(5)
C124	0.0389(6)	0.373(1)	0.0339(6)	5.7(5)
C125	0.0338(6)	0.4322(7)	0.0979(8)	6.4(6)
C126	0.0446(7)	0.385(1)	0.1659(6)	5.6(6)
D	6.061(7)	x^{1}	0.0497(4)	
E	1.632(8)	y^{1}	0.3254(6)	
F	3.599(8)	z^{1}	0.1019(5)	
C131	0.1620(8)	0.2692(8)	0.2818(9)	2.6(4)
C132	0.201(1)	0.3252(9)	0.2308(6)	3.2(4)
C133	0.2614(8)	0.3746(8)	0.253(1)	5.3(4)

(Table continued)

Table 29 continued 128

Name	x	y	z	B
C134	0.2830(8)	0.3680(8)	0.3254(9)	4.6(5)
C135	0.244(1)	0.3119(9)	0.3763(6)	6.1(5)
C136	0.1837(8)	0.2625(8)	0.355(1)	5.7(5)
D	0.979(6)	x^1	0.2225(4)	
E	1.97(1)	y^1	0.3186(5)	
F	5.34(1)	z^1	0.3036(4)	
C211	0.2396(6)	0.0633(8)	0.220(1)	2.9(4)
C212	0.232(1)	0.0852(8)	0.1451(7)	3.8(4)
C213	0.282(1)	0.1424(8)	0.1081(8)	5.7(5)
C214	0.3401(6)	0.1777(8)	0.146(1)	4.8(5)
C215	0.348(1)	0.1559(8)	0.2201(7)	3.1(4)
C216	0.298(1)	0.0987(8)	0.2571(8)	3.5(3)
D	1.017(6)	x^1	0.2899(4)	
E	2.01(1)	y^1	0.1205(5)	
F	4.58(1)	z^1	0.1826(4)	
C221	0.1885(8)	-0.1394(8)	0.2047(9)	2.9(4)
C222	0.1481(7)	-0.1499(9)	0.1420(6)	4.4(5)
C223	0.1593(9)	-0.233(1)	0.0939(5)	6.3(5)
C224	0.2109(8)	-0.3064(8)	0.1085(9)	6.5(5)
C225	0.2513(7)	-0.2959(9)	0.1712(6)	5.9(5)
C226	0.2401(9)	-0.212(1)	0.2193(5)	5.0(5)
D	2.548(7)	x^1	0.1997(4)	
E	2.239(9)	y^1	-0.2229(6)	
F	4.305(9)	z^1	0.1566(4)	

Table 29 continued

Name	x	y	z	B
C231	0.204(2)	-0.044(1)	0.356(1)	3.7(4)
C232	0.268(1)	-0.087(1)	0.372(1)	7.3(6)
C233	0.2879(6)	-0.104(1)	0.445(2)	7.8(6)
C234	0.244(2)	-0.076(1)	0.502(1)	6.5(6)
C235	0.180(1)	-0.032(1)	0.486(1)	7.2(6)
C236	0.1601(6)	-0.016(1)	0.413(2)	5.1(5)
D	1.986(8)	x^1	0.2240(5)	
E	1.51(2)	y^1	-0.0599(6)	
F	5.91(2)	z^1	0.4289(5)	
C311	-0.0533(6)	-0.1085(9)	0.3436(8)	2.9(4)
C312	-0.0379(5)	-0.0402(8)	0.4012(5)	3.5(4)
C313	-0.0876(8)	-0.0167(8)	0.4537(7)	4.5(4)
C314	-0.1527(6)	-0.0613(9)	0.4486(8)	4.8(5)
C315	-0.1682(5)	-0.1295(8)	0.3911(5)	4.2(4)
C316	-0.1185(8)	-0.1531(8)	0.3385(7)	3.6(4)
D	0.887(7)	x^1	-0.1030(4)	
E	0.51(1)	y^1	-0.0849(5)	
F	5.94(1)	z^1	0.3961(4)	
C321	0.0649(6)	-0.2422(8)	0.3208(8)	3.6(4)
C322	0.0965(9)	-0.320(1)	0.2785(4)	3.6(4)
C323	0.1365(6)	-0.3968(8)	0.3121(8)	4.8(5)
C324	0.1449(6)	-0.3965(8)	0.3880(8)	4.7(5)

Table 29 continued

Name	x	y	z	B
C325	0.1133(9)	-0.319(1)	0.4304(4)	6.2(5)
C326	0.0733(6)	-0.2419(8)	0.3968(8)	4.6(4)
D	2.521(7)	x^1	0.1049(3)	
E	1.691(9)	y^1	-0.3194(5)	
F	5.239(9)	z^1	0.3544(4)	
C331	-0.0278(6)	-0.212(1)	0.2037(6)	3.9(4)
C332	-0.0329(6)	-0.1672(7)	0.1340(9)	5.0(5)
C333	-0.0650(7)	-0.222(1)	0.0775(6)	8.0(6)
C334	-0.0921(6)	-0.322(1)	0.0906(6)	7.7(6)
C335	-0.0870(6)	-0.3669(7)	0.1603(9)	5.5(5)
C336	-0.0549(7)	-0.312(1)	0.2168(6)	4.4(4)
D	3.566(7)	x^1	-0.0599(4)	
E	1.851(8)	y^1	-0.2671(7)	
F	3.725(9)	z^1	0.1471(5)	

‡ These values are the coordinates of the ring center of gravity.

(Table continued)

Table 29 continued

(b)   Phenyl Hydrogen Rigid Bodies

Name	x	y	z	B
H112	0.077	0.416	0.322	8.3
H113	0.004	0.501	0.410	9.4
H114	-0.091	0.408	0.462	6.5
H115	-0.112	0.229	0.427	5.2
H116	-0.039	0.144	0.340	4.2
D	0.318			
E	0.669			
F	6.830			
H122	0.077	0.142	0.109	4.2
H123	0.059	0.223	-0.008	6.7
H124	0.031	0.407	-0.015	6.4
H125	0.022	0.509	0.095	6.9
H126	0.041	0.427	0.212	6.3
D	6.061			
E	1.632			
F	4.646			
H132	0.186	0.331	0.179	3.5
H133	0.290	0.416	0.218	5.9
H134	0.326	0.403	0.343	5.9
H135	0.259	0.305	0.429	6.6
H136	0.155	0.221	0.391	6.3

Table 29 continued

Name	x	y	z	B
D	0.979			
E	1.97			
F	6.39			
H212	0.190	0.060	0.118	4.0
H213	0.277	0.158	0.054	6.0
H214	0.376	0.219	0.119	5.2
H215	0.390	0.181	0.247	3.3
H216	0.303	0.083	0.310	4.0
D	1.017			
E	2.01			
F	5.62			
H222	0.111	-0.097	0.132	4.8
H223	0.130	-0.241	0.049	6.7
H224	0.219	-0.366	0.074	7.1
H225	0.288	-0.349	0.181	6.9
H226	0.269	-0.205	0.264	5.5
D	2.548			
E	2.239			
F	5.350			
H232	0.300	-0.107	0.331	7.5
H233	0.334	-0.135	0.457	8.6
H234	0.257	-0.087	0.554	7.1

Table 29 continued

Name	x	y	z	B
H235	0.148	-0.012	0.527	7.6
H236	0.114	0.015	0.402	5.6
D	1.986			
E	1.51			
F	6.96			
H312	0.009	-0.008	0.405	3.8
H313	-0.077	0.032	0.495	4.7
H314	-0.188	-0.045	0.486	5.1
H315	-0.215	-0.162	0.387	4.8
H316	-0.130	-0.202	0.297	4.0
D	0.887			
E	0.51			
F	6.99			
H322	0.091	-0.321	0.224	4.0
H323	0.160	-0.453	0.283	5.2
H324	0.173	-0.451	0.414	5.2
H325	0.119	-0.318	0.486	6.7
H326	0.050	-0.186	0.427	5.1
D	2.521			
E	1.691			
F	6.286			

Table 29 continued

Name	x	y	z	B
H332	-0.013	-0.096	0.124	5.6
H333	-0.069	-0.191	0.027	9.0
H334	-0.115	-0.363	0.050	8.5
H335	-0.107	-0.439	0.170	6.4
H336	-0.051	-0.343	0.267	4.7
D	3.566			
E	1.851			
F	4.772			

Table 30

Anisotropic Temperature Factors ($\mathring{A}^2 \times 10^3$)

Name	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	24.6(6)	27.3(6)	38.6(7)	-0.4(6)	0(1)	0(1)
Cℓ	30(3)	48(3)	69(3)	1(2)	-11(3)	6(2)
P1	32(3)	34(2)	45(3)	-1(2)	- 3(4)	-5(4)
P2	26(2)	35(2)	46(4)	0(2)	3(3)	-3(4)
P3	34(3)	25(2)	44(4)	-3(2)	0(3)	0(2)

Table 31

Selected Interatomic Distances

Atom 1	Atom 2	Distance (Å)	
Rh	Cℓ	2.404(4)	2.416(4)*
Rh	P1	2.304(4)	2.307(4)*
Rh	P2	2.225(4)	2.228(4)*
Rh	P3	2.338(4)	2.341(4)*
P1	C111	1.84(1)	
P1	C121	1.83(1)	
P1	C131	1.836(9)	
P2	C211	1.841(9)	
P2	C221	1.85(1)	
P2	C231	1.87(1)	
P3	C311	1.856(9)	
P3	C321	1.847(9)	
P3	C331	1.83(1)	

* value corrected for riding

Table 32

Selected Interatomic Angles

Atom 1	Atom 2	Atom 3	Angle (°)
P1	Rh	P2	97.7(1)
P1	Rh	P3	159.1(2)
P1	Rh	Cℓ	85.3(1)
P1	Rh	H222	122.9
P2	Rh	P3	96.4(2)
P2	Rh	Cℓ	166.7(2)
P2	Rh	H222	66.1
P3	Rh	Cℓ	84.5(1)
P3	Rh	H122	77.1
Cℓ	Rh	H122	101.3
Rh	P1	C111	112.5(5)
Rh	P1	C121	114.3(5)
Rh	P1	C131	123.4(4)
Rh	P2	C211	119.0(4)
Rh	P2	C221	109.9(5)
Rh	P2	C231	116.4(5)
Rh	P3	C311	104.4(4)
Rh	P3	C321	122.3(4)
Rh	P3	C331	120.6(5)
P1	C111	C114	178.7(8)
P1	C121	C124	175.1(8)
P1	C131	C134	177.3(6)

(Table continued)

Table 32

Selected Interatomic Angles

Atom 1	Atom 2	Atom 3	Angle (°)
P1	Rh	P2	97.7(1)
P1	Rh	P3	159.1(2)
P1	Rh	Cℓ	85.3(1)
P1	Rh	H222	122.9
P2	Rh	P3	96.4(2)
P2	Rh	Cℓ	166.7(2)
P2	Rh	H222	66.1
P3	Rh	Cℓ	84.5(1)
P3	Rh	H122	77.1
Cℓ	Rh	H122	101.3
Rh	P1	C111	112.5(5)
Rh	P1	C121	114.3(5)
Rh	P1	C131	123.4(4)
Rh	P2	C211	119.0(4)
Rh	P2	C221	109.9(5)
Rh	P2	C231	116.4(5)
Rh	P3	C311	104.4(4)
Rh	P3	C321	122.3(4)
Rh	P3	C331	120.6(5)
P1	C111	C114	178.7(8)
P1	C121	C124	175.1(8)
P1	C131	C134	177.3(6)

(Table continued)

Table 32 continued

Atom 1	Atom 2	Atom 3	Angle (°)
P2	C211	C214	174.6(7)
P2	C221	C224	174.3(8)
P2	C231	C234	176.4(9)
P3	C311	C314	177.6(7)
P3	C321	C324	177.4(7)
P3	C331	C334	178.1(9)
C111	P1	C121	104.1(5)
C111	P1	C131	98.5(6)
C121	P1	C131	101.5(6)
C211	P2	C221	97.2(6)
C211	P2	C231	103.5(6)
C221	P2	C231	108.9(6)
C311	P3	C321	102.6(5)
C311	P3	C331	104.2(6)
C321	P3	C331	100.2(6)

Table 33

Selected Intermolecular Contacts

Atom 1	Atom 2	Symmetry Operation (on atom 2)	Distance ($\overset{\circ}{A}$)
H112	H323	x,y+1,z	2.41
H113	H124	$\overline{x},\overline{y}+1,1/2+z$	1.92
H123	H326	$\overline{x},\overline{y},1/2+z-1$	2.48
H212	H314	$\overline{x},\overline{y},1/2+z-1$	2.40
H213	H325	$1/2-x,1/2+y,1/2+z-1$	2.41
H214	H325	$1/2-x,1/2+y,1/2+z-1$	2.47

Table 34

Selected Intramolecular Non-Bonded Contacts

Atom 1	Atom	Distance (Å)
Rh	H222	2.84
Rh	H236	2.94
Rh	H122	2.96
Rh	H116	2.96
P1	Cℓ	3.190(6)
P3	Cℓ	3.188(6)
P1	P2	3.411(5)
P2	P3	3.404(6)
H112	H126	2.12
H226	H232	1.84
H236	H312	2.07
C131	C211	3.22(1)
C133	C215	3.30(1)
C221	C322	3.20(1)
C226	C322	3.29(1)
C236	C326	3.34(1)

Fig. 11

View Perpendicular to the P1-P2-P3 Plane
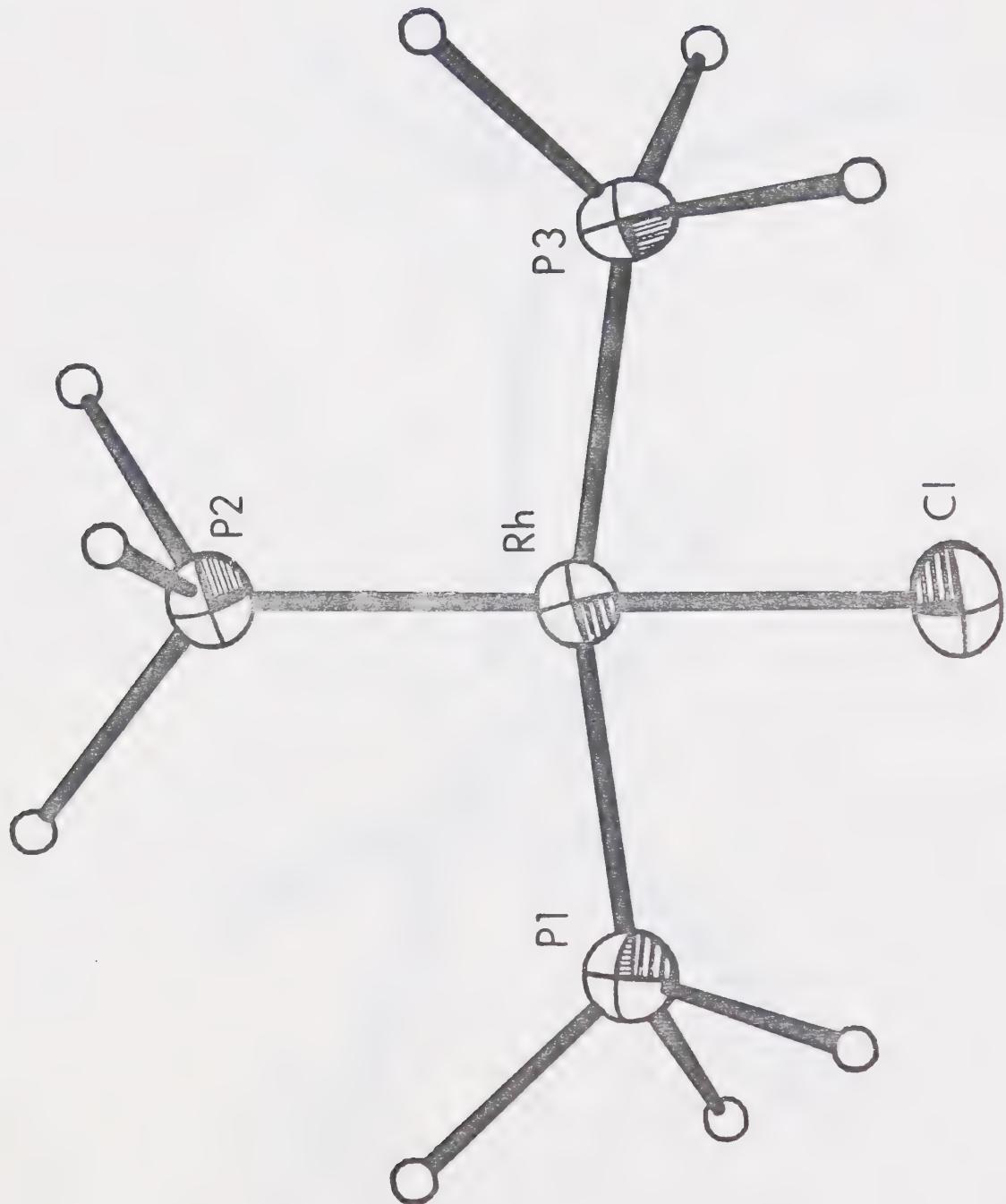
Fig. 12

Central Geometry Viewed down Pl-P3 Direction
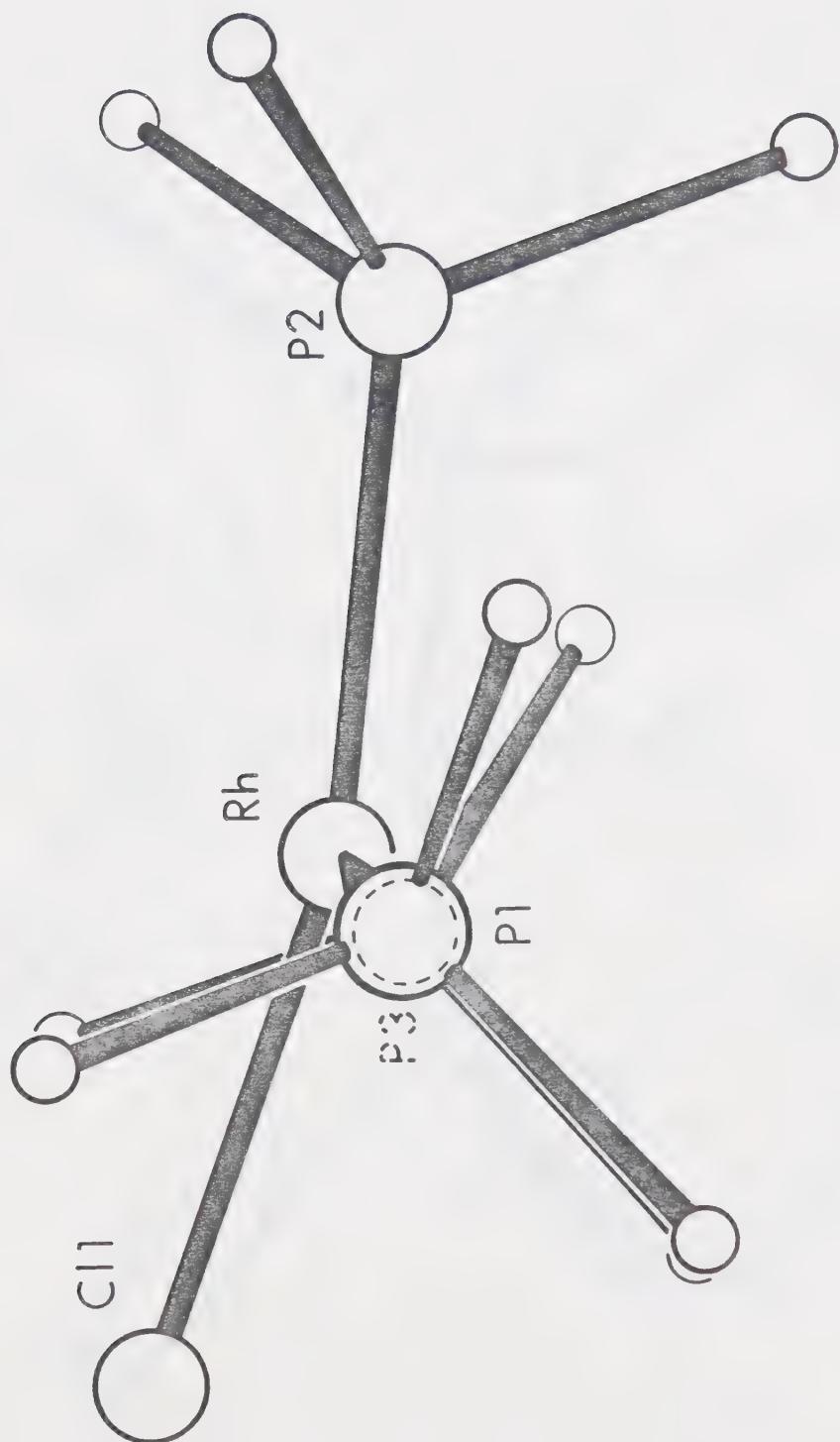
Fig. 13

A General View of $[RhCl(P(C_6H_5)_3)_3]$ (Orange Form)
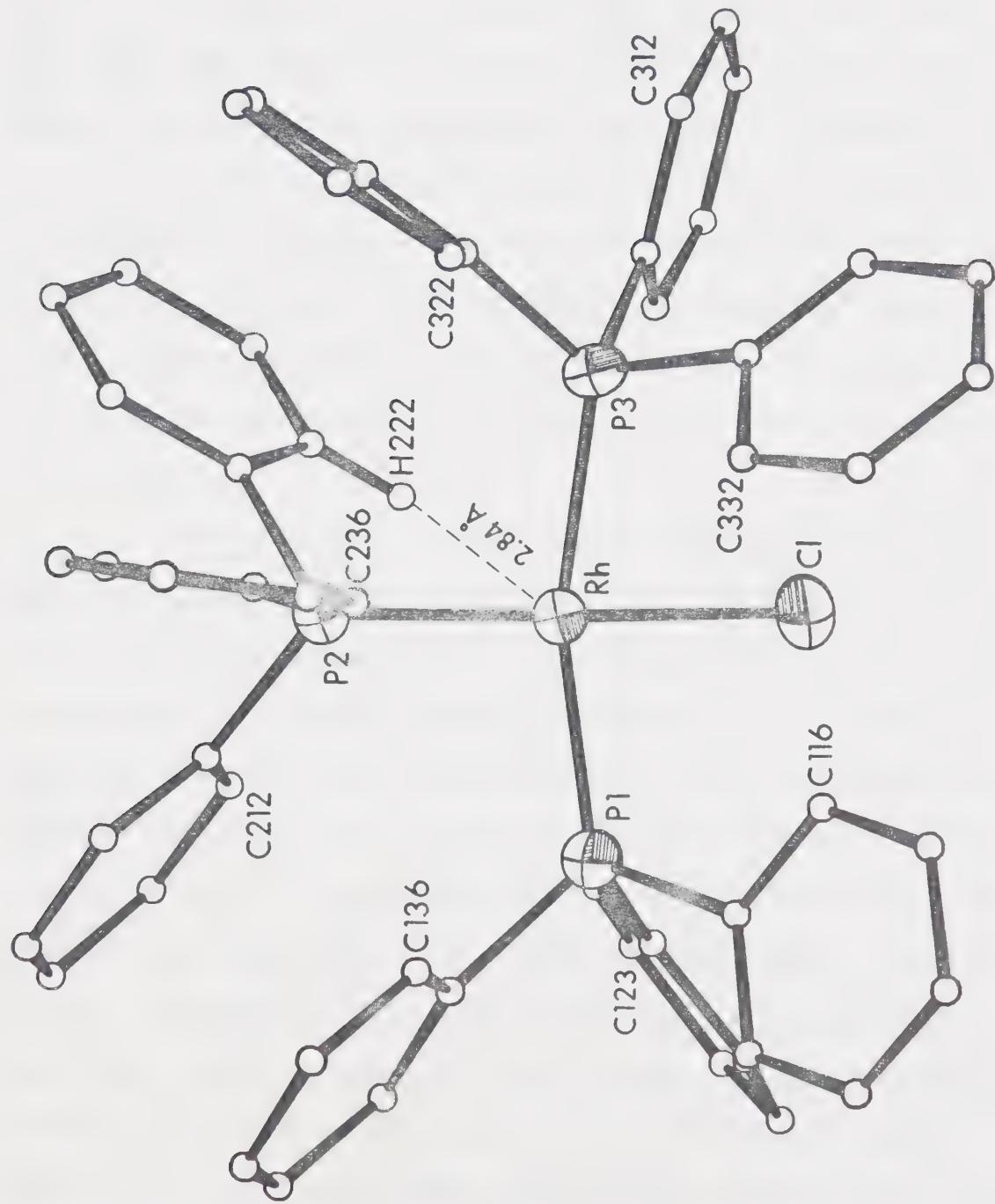
Discussion

To a first approximation the coordination of the rhodium atom (Fig. 11) is square planar but there is a marked distortion towards tetrahedral geometry as emphasized by Fig. 12 and the angles Cl-Rh-P2 and P1-Rh-P3 of 166.7(2)° and 159.1(2)° respectively. The latter angle cannot be interpreted simply as being due to the distortion towards a tetrahedral geometry since it contains a significant contribution from a bending of P1-Rh-P3 within the mean molecular plane of the complex. The distortions from square planar coordination are explained by the bulkiness of the triphenylphosphine ligands *(vide infra)*.

The phosphorus atoms can be grouped chemically into two categories, (1) one pair mutually *trans* and *cis* to the chlorine atom, and (2) the unique phosphorus *trans* to chlorine. For this latter phosphorus, the rhodium - phosphorus bond length is 2.228(4) Å which is significantly shorter than the other two bond lengths (Rh-P1, 2.307(4), Rh-P3, 2.341(4) Å) between rhodium and the mutually *trans* phosphorus atoms (Δ/σ: 14 and 19 respectively). This pattern of rhodium-phosphorus bond lengths is consistent with the π-acidity and thus *trans* effect of phosphorus being greater than that of chlorine [137-141]. The difference between the chemically equivalent rhodium-phosphorus bond lengths appears to be statistically significant (Δ/σ,6)

and may reflect differences in intra ligand contacts.
The difference may not be significant in that the standard
deviations as derived must underestimate the true values
if systematic errors are present.

The average phosphorus-carbon bond length in
this structure is 1.844 Å and is somewhat longer than the
value observed for triphenylphosphine [129] and its typical
metal complexes [17,18] (~1.83Å). This increase appears to
be correlated to the short rhodium-phosphorus bonds. If
the phosphorus-carbon bond lengths are sorted according
to the phosphorus atom then the bonds involving P1 and P3
average 1.838 Å while those involving P2 average 1.855 Å.
An analysis of the six phosphorus-carbon bonds involving
P1 and P3 shows that they are consistent with a standard
deviation of 0.010 Å which is in remarkable agreement with
the standard deviations derived *via* the least squares
refinement and ORFFE II. The P2-carbon distances show a
maximum deviation from their mean 1.6σ. The difference
between the group averages is interesting but not accept-
able as statistically significant by normal conservative
crystallographic criteria. It was this feature which lead
to the redetermination of the structure of the red form
(Chapter VI) since it might provide independent evidence
of the observed trend and averaging the values of both
structures might produce a significant variation in
distances.

The rhodium-chlorine bond length agrees well
with those observed for the dioxygen derivatives described
in Chapters III and IV but appears to be rather longer than
the values as reported by Mason *et al.*, [138] for the red
form of $RhCl(P(C_6H_5)_3)_3$, (2.373(8), 2.381 [140] Å) and
$RhCl(C_2F_4)(P(C_6H_5)_3)_2$, (2.375(8) Å). This topic is dis-
cussed in more detail in Chapter VI.

The final structural detail to be discussed is
the close rhodium-H222 contact of 2.84 Å which is evident
in Fig. 13. This close contact could result from (1)
natural attraction of the hydrogen for the rhodium atom,
or (2) a repulsion elsewhere in the molecule [139]. Table
33 contains all important intramolecular non-bonded con-
tacts. In this Table if one ignores contacts between
carbon atoms of the type (M11),(M21),(M31) then there are
surprisingly few contacts between phenyl groups that are
significantly less than the sum of the van der Waals radii.
These contacts are: H112-H126, 2.12 Å: H226-H232, 1.84 Å;
H236-H312, 2.07 Å; C131-C211, 3.22(1) Å; C133-C215,
3.30(1) Å; C221-C322, 3.20(1) Å; C226-C322, 3.29 Å; C236-
C326, 3.34 Å. From these contacts it is obvious that
phenyl group 22 is repelled by H232 and C322 into close
contact with the rhodium atom i.e. the short rhodium
hydrogen contact cannot be treated as representing an
attractive force. Rather it represents a balance of
repulsive forces. There is also a larger number of

repulsions involving the atoms of the phenyl groups attached to P3 relative to the number of repulsions involving the atoms of the phenyl rings attached to P1. Thus one could explain the slight increase of bond length for Rh-P3 when compared to Rh-P1. It is highly doubtful that the interligand repulsions lead to the apparently abnormal phosphorus-carbon bond lengths in this structure. This view is discussed further in Chapter VI.Intermolecular contacts are listed in Table 32. Only one of these contacts is abnormally short *viz*. H113 at x,y,z to H124 at $\bar{x}$, 1-y, 1/2+z of 1.92 Å. All other contacts are equal to or greater than the sum of the van der Waals radii and further discussion is not warranted.

CHAPTER VI

The Crystal and Molecular Structures of

the Red Form of $RhCl(P(C_6H_5)_3)_3$.

Experimental

Dark red crystals of the compound were examined under a polarizing microscope and found to be chunky, capped prisms, with no sign of twinning being evident. A crystal was mounted on the end of a thin glass fibre and a Laué photograph taken. Again no crystal defects were noticed and the crystal appeared to be suitable for a diffraction study. Preliminary Weissenberg and precession photographs indicated that the compound crystallized in the orthorhombic crystal system (Laué symmetry mmm). The systematic absences ($0kl$, $k + l = 2n + 1$; $h0l$, $h = 2n + 1$) were consistent with the spacegroups $Pna2_1$ or Pnam.

Precise lattice parameters were obtained from a least squares refinement using 2θ values of 18 accurately centered high angle reflections (CuKα_1 1.54051 Å) as: a, 32.96(1); b, 12.271(2); C, 11.013(1) Å. All reflections used showed resolvable splitting of the α_1/α_2 peaks. The density of the compound was measured by flotation in aqueous potassium iodide solution as $\rho_{obs} = 1.382$ g-cm^3, a value in good agreement with that calculated using precise lattice parameters, $\rho_{calc} =$

1.379 g-cm^{-3} (for 4 molecules per unit cell).

Intensity data were collected on a Picker manual diffractometer with the crystal "b" axis aligned coincident with the diffractometer ϕ axis. Copper k$\bar{\alpha}$ X-radiation was used with a graphite monochromator (002 reflecting plane) and a 2° takeoff angle. Diffractometer settings were calculated using the programme MIXG2 and the high intensity axial peaks were scanned at expanded chart speeds to detect twinning or unusual reflection shape. No unusual effects were found. Each reflection was scanned from $(2\theta - 1)°$ to $(2\theta + 1)°$ in 1 minute and 20 second stationary background counts were taken at the limits of the coupled $\omega/2\theta$ scan. The total background counts were calculated from a linear interpolation of the two stationary counts. Data were only measured to 90° in 2θ because of the rapid decrease in intensities with increasing 2θ as observed in the preliminary photographic study. During the data collection 5 reflections were measured at 8 hour intervals to check against crystal misalignment and/or decomposition. No significant changes in these intensities were found throughout the entire data collection. A total of 2221 reflections were measured and of this number 1469 were statistically reliable using the criterion $I < 3\sigma$ for rejection. Reflections having a maximum count rate in excess of 10^4 counts-sec^{-1} (and thus

greater than the linear response of the scintillation counter) were recollected at the end of the initial data collection at reduced voltages and scaled into the data by comparison with the other reflections of lower intensity, recollected under the same conditions. The 0k0 reflections were measured at 10° intervals in ϕ to provide experimental verification of absorption corrections.

The crystal faces were identified as members of the forms {100}, {210}, {201} and the crystal was removed from the diffractometer. The crystal dimensions (0.17 x 0.21 x 0.14 mm) were measured under a calibrated microscope. These values were used to make an absorption correction ($\mu_{K\bar{\alpha}}$ = 47.6 cm^{-1}) and the data for different ϕ values after correction for absorption were consistent within 5%. Transmission factors varied from 0.683 to 0.566. Reflection data were corrected for Lorentz and polarization effects and the structure amplitudes with their respective standard deviations calculated using an uncertainty factor of 0.03. Only the significant data were used in the structure solution and refinement.

Solution of Structure and Refinement

A Patterson map was calculated and the molecule was assumed to have the more general space group Pna2$_1$

for reasons outlined in Chapter V. The Harker lines gave
peaks representing the rhodium-rhodium intermolecular
vectors and the rhodium "x" and "y" coordinates were
obtained. The "z" coordinate of the rhodium atom was set
at 0.25 to fix the origin in this direction. The atomic
coordinates of the chlorine atom were found from the intra-
molecular vectors and checked with the Harker line peaks
for this atom (see Table 35). The remaining atoms were
identified in a series of electron density difference maps
as indicated in Table 36.

The rigid body description for the carbon atoms
of the phenyl groups was used to minimize the number of
parameters. The atomic scattering factors for the rhodium,
chlorine, phosphorus and carbon atoms were for neutral
species. These were derived from Cromer's coefficients [111]
and included (for rhodium, chlorine and phosphorus) the
real and imaginary terms for anomalous dispersion.
Hydrogen atoms were added to the refinement at their cal-
culated positions with carbon-hydrogen bond lengths of
1.0 Å and isotropic temperature factors 10% greater than
those of the carbon atoms to which they were attached.
Hydrogen scattering factors were those of Mason and
Robertson [113].

Refinement of the completed structure was
routine (Table 37) except for problems caused by an error

in the refinement programme that was specific to noncentro-symmetric space groups. Elimination of this error allowed the structure to refine to convergence. As mentioned in Chapter v two solutions must be tested for this spacegroup when anomalous scattering is considered. When the molecule was reflected through the "xy" plane a Hamilton test showed that the new model was preferred at better than the 99.5% confidence level.

At convergence (estimated standard deviation of an observation of unit weight = 1.595; maximum shift/ σ = 0.02; R_1 = 0.042; R_2 = 0.045) a final electron density difference map was calculated and the correlation matrix printed. Examination of the electron density map showed the largest positive and negative peaks (0.38 e.$\overset{\circ}{A}^{-3}$ and -0.20 e.$\overset{\circ}{A}^{-3}$; cf. carbon ~3e.$\overset{\circ}{A}^{-3}$) to be situated near phenyl groups. The correlation matrix showed high cor-relations between some phenyl carbon temperature factors, but all coordinate interactions were less than 0.18.

All interatomic bond lengths, inter- and intra-molecular contacts (with their angles and standard devi-ations) to a distance of 3.5 $\overset{\circ}{A}$ were calculated using ORFFE II. Bond lengths involving the rhodium atom were also calculated to include a correction for thermal motion assuming the lighter atoms to ride on the heavier rhodium atom.

Table 35

Assignment of Patterson Map Peaks

Peak Coordinates			Rel. Height (origin=999)	Assignment	Calc. Height	Calc. Coordinates (from Solution)		
u	v	w						
0.504,	0.204,	0.000	295	$1/2, 1/2-2y_a, 0$	198	0.500,	0.256,	0.000
0.270,	0.504,	0.494	285	$1/2-2x_a, 1/2, 1/2$	198	0.274,	0.500,	0.500
0.225,	0.240,	0.494	167	$2x_a, 2y_a, 1/2$	99	0.226,	0.244,	0.500
0.347,	0.504,	0.494	78	$1/2-2x_b, 1/2, 1/2$	28	0.346,	0.500,	0.500
0.504,	0.312,	0.000	60	$1/2, 1/2-2y_b, 0$	28	0.500,	0.322,	0.000
0.148,	0.176,	0.494	40	$2x_b, 2y_b, 1/2$	14	0.154,	0.178,	0.500
0.036,	0.020,	0.182	43	$x_a-x_b, y_a-y_b, z_a-z_b$	37	0.036,	0.033,	0.184
0.309,	0.480,	0.312	34	$1/2-x_a-x_b, 1/2-y_a+y_b, 1/2-z_a+z_b$	37	0.310,	0.467,	0.316
0.462,	0.288,	0.182	31	$1/2-x_a+x_b, 1/2-y_a-y_b, z_a-z_b$	37	0.464,	0.289,	0.184
0.193,	0.216,	0.312	29	$x_a+x_b, y_a+y_b, 1/2-z_a+z_b$	37	0.190,	0.211,	0.316

Assignment Results

		x	y	z
a = Rh		0.113	0.122	-0.250
b = Cℓ		0.077	0.089	-0.434

Table 36

Structure Solution Sequence

Refinement Cycle	Atoms used in Phasing	R_1	Atoms Located in Diff. Map
1	Rh,Cℓ	0.427	P1,P2,P3
2	Rh,Cℓ,P1,P2,P3	0.326	
3	·· ·· ·· ·· ·· ··	0.281	C111–C116,C131–C136,C221–C226, C331–C336
4	Rh,Cℓ,P1,P2,P3,C111–C116, C131–C136,C221–C226,C331–C336	0.262	
5	·· ·· ·· ·· ·· ·· ··	0.245	C121–C126,C211–C216,C231–C236, C311–C316,C321–C326

Table 37

Refinement Sequence for Model

Refinement Cycle		R_1	R_2
6	All atoms except hydrogens included, temperature factors held constant (B:Rh, 2.5; Cℓ, 2.5; P, 3.0; C, 5.0)	0.201	0.220
7	.. ..	0.172	0.193
8	temperature factors refined	0.147	0.164
9	.. ..	0.112	0.129
10	anomalous dispersion correction applied	0.097	0.107
11	central atoms given anisotropic temperature factors	0.079	0.086
12	hydrogen atoms included	0.072	0.078
13	error in refinement programme corrected	0.047	0.056
14	origin molecule reflected through "xy" plane	0.044	0.047
15	.. ..	0.042	0.044

Results

The observed and calculated structure amplitudes ($|F_o|$) and $|F_c|$ respectively) are listed in Table 38. Table 39 gives the atomic coordinates of all atoms with the anisotropic thermal parameters of the central atoms being included in Table 40. The interatomic angles and distances are given in Tables 41 and 42 respectively with the inter- and intramolecular non-bonded contacts being listed in Tables 43 and 44. The standard deviations of the least significant digit are included in parentheses.

Fig. 14 shows the general geometry of the molecule whilst Figs. 15 and 16 show views down the P1-P3 direction and perpendicular to the P1-P2-P3 plane.

Table 38

Observed and Calculated Structure Amplitudes (electronsx10)

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 0**				12	3	571	553	17	6	484	481	5	1	343	335	4	4	465	465
2	0	364	361	13	3	381	384	19	6	728	750	6	1	1414	1432	5	4	301	278
4	0	2344	2418	15	3	364	371	21	6	303	257	7	1	2074	2034	6	4	1142	1158
6	0	393	394	16	3	773	844	23	6	578	568	8	1	672	678	7	4	1456	1466
8	0	980	987	17	3	484	480	25	6	582	594	9	1	1347	1362	8	4	1325	1317
10	0	1248	1267	19	3	870	808	2	7	928	960	10	1	907	912	9	4	497	498
12	0	422	457	20	3	570	559	3	7	422	446	11	1	1325	1343	10	4	941	933
14	0	468	497	21	3	262	337	4	7	1114	1162	12	1	741	769	11	4	551	540
16	0	744	720	23	3	254	276	5	7	780	828	13	1	264	300	12	4	858	893
18	0	851	777	24	3	398	421	6	7	838	785	14	1	830	863	13	4	284	313
20	0	903	1071	25	3	279	315	7	7	638	568	15	1	893	965	14	4	405	477
22	0	1282	1366	26	3	391	401	8	7	965	919	17	1	701	691	15	4	527	499
24	0	563	529	27	3	364	351	9	7	328	294	18	1	958	938	16	4	1006	1041
26	0	1191	1224	0	4	1549	1550	10	7	703	766	19	1	809	803	17	4	369	395
28	0	702	667	1	4	415	424	12	7	419	466	20	1	493	569	20	4	917	889
30	0	452	485	2	4	365	386	13	7	326	365	21	1	568	585	21	4	264	301
1	1	1531	1531	3	4	303	318	14	7	686	663	22	1	786	788	23	4	412	414
2	1	1660	1670	4	4	2986	3102	15	7	600	627	23	1	609	613	24	4	635	660
3	1	1508	1588	5	4	1410	1431	17	7	286	323	25	1	319	348	25	4	276	227
4	1	669	694	6	4	265	341	20	7	315	335	26	1	502	452	27	4	365	376
5	1	748	791	7	4	617	605	23	7	461	429	27	1	372	397	28	4	639	654
6	1	779	662	8	4	1155	1135	0	8	967	941	28	1	560	589	0	5	1125	1130
7	1	2682	2709	9	4	1020	995	2	8	365	337	29	1	470	477	1	5	1289	1241
8	1	2049	2015	10	4	329	345	4	8	857	888	1	2	410	427	2	5	284	308
9	1	681	669	11	4	390	360	6	8	642	687	2	2	577	564	3	5	1291	1294
10	1	240	229	12	4	465	468	7	8	307	304	3	2	553	562	4	5	1140	1144
11	1	827	833	13	4	807	785	8	8	504	452	4	2	675	658	5	5	303	276
12	1	880	876	14	4	880	889	10	8	501	469	5	2	989	953	7	5	863	881
13	1	1006	1025	15	4	364	392	11	8	716	760	6	2	439	408	8	5	747	756
14	1	466	398	17	4	675	721	14	8	330	335	7	2	733	730	9	5	684	644
15	1	212	218	18	4	1024	1105	18	8	390	417	9	2	1183	1170	10	5	408	409
16	1	351	362	22	4	794	786	19	8	282	223	10	2	622	610	11	5	1113	1126
17	1	1065	1112	25	4	431	412	4	9	313	285	11	2	514	543	12	5	898	933
18	1	658	614	26	4	569	502	5	9	447	403	12	2	405	433	13	5	197	130
19	1	677	715	27	4	322	386	6	9	770	765	13	2	1133	1119	14	5	968	1003
20	1	976	1011	28	4	256	232	7	9	262	255	14	2	767	761	15	5	690	668
21	1	497	495	1	5	1430	1374	9	9	1032	1065	15	2	1340	1347	16	5	310	332
22	1	546	548	2	5	1424	1364	10	9	616	638	16	2	388	390	17	5	301	244
23	1	470	499	3	5	944	985	12	9	324	338	17	2	789	806	18	5	964	1004
24	1	823	830	4	5	314	350	13	9	665	666	18	2	224	232	19	5	436	408
25	1	706	697	5	5	1629	1704	14	9	302	219	19	2	1108	1088	20	5	228	228
28	1	324	294	6	5	1256	1321	16	9	629	612	20	2	291	326	21	5	401	455
30	1	584	587	7	5	634	666	0	10	295	230	21	2	674	665	22	5	512	515
0	2	464	470	9	5	1051	1037	1	10	235	192	23	2	585	582	23	5	588	587
1	2	189	209	11	5	353	325	3	10	402	407	25	2	251	233	24	5	351	363
2	2	538	568	12	5	837	771	5	10	352	356	26	2	318	309	25	5	654	675
3	2	345	376	13	5	377	401	7	10	827	848	27	2	437	447	1	6	943	939
5	2	1145	1137	14	5	348	288	9	10	595	600	29	2	280	177	2	6	800	804
6	2	2736	2758	15	5	219	251	10	10	360	436	0	3	971	981	3	6	602	617
7	2	1670	1636	16	5	865	933	11	10	1471	1484	1	3	1069	1062	4	6	845	862
8	2	953	956	17	5	443	480	2	11	702	743	2	3	989	1008	5	6	1258	1302
9	2	203	136	19	5	236	235	3	11	288	314	3	3	723	683	7	6	308	319
10	2	257	145	20	5	843	825	4	11	325	315	5	3	1606	1590	8	6	275	268
11	2	1140	1135	21	5	839	881	6	11	781	731	6	3	972	980	9	6	920	911
12	2	777	751	23	5	340	321	**L = 1****				7	3	784	780	10	6	908	895
13	2	884	877	24	5	367	469	2	0	3852	4048	8	3	482	479	11	6	226	207
14	2	223	207	25	5	279	302	4	0	1482	1503	10	3	707	663	12	6	311	346
15	2	754	784	26	5	307	316	6	0	548	450	11	3	723	731	13	6	1219	1235
16	2	333	317	27	5	823	774	8	0	1284	1276	12	3	500	487	14	6	351	326
17	2	749	742	0	6	368	371	10	0	790	807	13	3	395	408	17	6	978	974
19	2	977	935	1	6	611	651	12	0	639	594	14	3	900	678	19	6	355	326
20	2	227	277	2	6	663	653	14	0	415	425	15	3	396	460	20	6	301	297
21	2	791	775	3	6	1043	1099	16	0	428	480	16	3	247	290	21	6	708	669
23	2	666	686	4	6	187	223	18	0	897	871	17	3	548	555	22	6	269	274
29	2	361	295	5	6	556	561	20	0	1563	1596	18	3	815	823	23	6	471	472
1	3	2957	3019	6	6	567	600	22	0	536	555	19	3	427	421	0	7	656	663
2	3	1812	1804	7	6	1317	1334	24	0	1303	1287	21	3	667	656	1	7	512	477
3	3	1680	1639	8	6	514	528	26	0	507	530	22	3	669	669	2	7	228	166
5	3	630	661	10	6	411	449	28	0	552	588	23	3	371	358	3	7	506	511
6	3	441	469	11	6	1246	1235	30	0	581	644	24	3	297	323	4	7	762	754
7	3	575	596	12	6	278	280	0	1	2106	2148	25	3	381	373	6	7	570	596
8	3	1287	1260	13	6	402	383	1	1	1380	1401	28	3	323	357	7	7	354	363
9	3	493	493	14	6	302	294	2	1	647	655	1	4	355	403	8	7	527	549
10	3	624	618	15	6	1042	1051	3	1	1023	983	2	4	1507	1489	10	7	908	906
11	3	275	141	16	6	370	377	4	1	617	630	3	4	762	744	11	7	303	317

Table 38 continued

H	K	FOBS	FCAL
		L = 1	
12	7	710	721
13	7	311	330
14	7	509	501
16	7	343	.350
18	7	472	489
19	7	314	327
21	7	299	273
22	7	509	537
1	8	285	299
2	8	717	711
4	8	697	707
6	8	699	733
7	8	224	238
8	8	377	389
9	8	505	461
10	8	238	259
11	8	303	287
12	8	597	601
13	8	385	380
16	8	277	286
17	8	262	237
20	8	607	618
21	8	270	263
0	9	383	378
1	9	274	174
2	9	331	345
4	9	556	551
6	9	402	386
7	9	645	670
8	9	520	546
10	9	330	365
11	9	785	808
13	9	318	275
14	9	620	593
16	9	488	471
17	9	530	514
1	10	328	313
3	10	446	410
5	10	448	475
7	10	577	556
9	10	1205	1216
10	10	255	255
11	10	246	158
13	10	1244	1216
0	11	577	580
2	11	313	246
4	11	789	796
5	11	388	365
		L = 2	
0	0	2599	2608
2	0	393	369
4	0	664	663
6	0	1447	1461
8	0	1593	1609
10	0	1242	1265
12	0	2006	2066
14	0	654	654
16	0	960	935
18	0	1646	1632
20	0	478	488
22	0	1175	1254
26	0	663	627
28	0	372	266
1	1	1993	1941
2	1	1615	1550
3	1	629	651
4	1	1408	1320
5	1	1999	1932
6	1	743	699
7	1	702	715
8	1	1083	1078
9	1	962	949
10	1	595	596
11	1	196	233
12	1	720	727
13	1	1538	1548
14	1	732	735
15	1	540	673
16	1	509	529
17	1	1041	1020
19	1	600	618
20	1	756	778
21	1	548	560
23	1	387	402
24	1	602	553
25	1	423	487
26	1	407	382
27	1	411	401
28	1	357	410
0	2	618	603
1	2	1087	1044
2	2	1945	1868
3	2	709	720
4	2	328	320
5	2	1488	1450
6	2	318	299
7	2	1318	1304
8	2	705	709
9	2	817	819
10	2	282	255
11	2	1687	1637
12	2	1044	1002
13	2	538	529
14	2	302	292
15	2	838	874
17	2	1104	1166
18	2	400	460
19	2	450	423
20	2	252	257
21	2	939	959
23	2	307	247
24	2	378	403
25	2	616	605
29	2	608	598
1	3	885	841
2	3	1078	1077
3	3	595	605
4	3	775	786
5	3	630	637
6	3	848	840
7	3	170	151
8	3	339	311
9	3	913	896
10	3	1100	1108
11	3	416	409
12	3	578	611
13	3	477	491
14	3	215	248
15	3	463	447
16	3	996	983
17	3	804	757
18	3	505	514
19	3	719	736
20	3	777	727
21	3	447	512
22	3	435	427
23	3	421	468
26	3	280	291
27	3	431	425
28	3	339	289
0	4	787	782
1	4	199	195
2	4	575	545
3	4	747	715
4	4	1210	1150
5	4	422	427
6	4	769	797
7	4	370	329
8	4	983	973
9	4	475	465
10	4	837	802
11	4	570	561
12	4	1091	1075
14	4	1249	1236
15	4	336	264
16	4	480	455
17	4	438	415
18	4	1008	1010
19	4	305	289
20	4	391	421
21	4	407	395
22	4	682	722
26	4	612	603
27	4	330	356
1	5	811	804
2	5	775	807
3	5	1009	1023
5	5	770	768
6	5	1329	1340
7	5	406	348
9	5	1340	1308
10	5	1230	1159
11	5	304	273
12	5	757	732
13	5	971	946
14	5	737	748
16	5	835	849
17	5	576	603
19	5	385	419
20	5	838	501
21	5	742	761
22	5	310	329
23	5	518	503
24	5	333	353
25	5	251	215
0	6	972	946
1	6	1024	984
2	6	548	481
3	6	1385	1339
4	6	500	507
5	6	515	522
6	6	266	207
7	6	1263	1263
8	6	788	740
9	6	355	314
11	6	772	788
12	6	473	483
14	6	217	170
15	6	1062	1065
16	6	256	319
19	6	901	933
20	6	431	426
21	6	295	290
22	6	250	235
23	6	559	535
1	7	617	640
2	7	727	748
3	7	465	423
5	7	792	753
6	7	841	838
7	7	392	430
8	7	405	416
9	7	411	383
10	7	771	757
11	7	413	413
12	7	587	598
14	7	597	576
16	7	637	635
20	7	591	592
21	7	401	325
0	8	748	740
1	8	261	302
2	8	291	295
3	8	471	472
4	8	623	636
5	8	255	233
6	8	613	589
8	8	518	488
9	8	313	281
10	8	432	456
11	8	634	624
14	8	427	425
17	8	427	389
18	8	608	584
19	8	256	260
1	9	389	328
2	9	579	562
3	9	479	443
4	9	500	501
6	9	666	655
7	9	402	377
8	9	296	312
9	9	738	687
10	9	385	366
12	9	306	328
13	9	639	645
14	9	285	275
15	9	408	367
16	9	400	403
17	9	434	434
1	10	612	590
3	10	496	456
5	10	596	573
7	10	730	729
9	10	320	299
11	10	1183	1158
1	11	314	264
2	11	762	727
		L = 3	
2	0	2036	1985
4	0	801	800
6	0	1066	1049
8	0	1415	1396
10	0	1690	1694
12	0	1352	1365
14	0	1232	1262
16	0	613	613
18	0	574	616
20	0	1101	1098
24	0	900	827
26	0	383	309
28	0	523	470
0	1	383	394
1	1	549	559
2	1	387	394
3	1	1015	987
4	1	1086	1136
5	1	1020	1024
6	1	932	900
7	1	660	649
8	1	926	907
9	1	441	449
10	1	649	632
11	1	1651	1592
12	1	845	831
15	1	1395	1419
17	1	431	442
18	1	478	457
19	1	482	817
22	1	642	662
23	1	346	356
24	1	288	260
25	1	374	375
26	1	471	430
27	1	257	296
28	1	360	341
1	2	556	567
2	2	476	484
3	2	665	660
4	2	675	730
5	2	871	844
6	2	1053	1061
7	2	825	781
8	2	233	213
9	2	1432	1444
10	2	699	675
11	2	359	380
12	2	233	225
13	2	1382	1369
15	2	433	448
16	2	442	432
17	2	568	559
18	2	377	436
19	2	902	665
20	2	284	315
21	2	415	376
23	2	758	761
26	2	393	374
27	2	684	693
0	3	416	413
1	3	525	524
2	3	246	192
3	3	816	842
4	3	580	579
5	3	207	213
6	3	807	812
7	3	1080	1052
8	3	1137	1120
9	3	269	259
10	3	868	905
11	3	618	614
12	3	802	800
13	3	413	386
14	3	876	887
15	3	802	826
17	3	317	330
18	3	881	795
19	3	351	391
20	3	718	762
21	3	461	439
23	3	389	388
24	3	493	534
25	3	509	441
1	4	265	242
2	4	260	260
3	4	376	401
4	4	378	373
5	4	741	715
6	4	1309	1278
8	4	709	653
9	4	629	608
10	4	1410	1442
11	4	287	251
12	4	957	966
14	4	752	703
15	4	285	302
16	4	1299	1275
18	4	241	213
19	4	488	484
20	4	766	743
24	4	418	395
0	5	1022	1088
1	5	989	950
3	5	917	896
4	5	672	648
5	5	425	421
6	5	296	352
7	5	936	903
8	5	988	1001
10	5	555	541
11	5	854	877
12	5	989	978
14	5	644	620
15	5	731	750

Table 38 continued

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
L = 3**				6	0	1525	1515	22	3	468	456	0	8	517	532	12	2	209	193
16	5	702	655	8	0	1477	1445	23	3	389	377	2	8	312	301	13	2	767	749
17	5	310	320	10	0	1204	1198	24	3	248	152	3	8	246	140	14	2	229	245
18	5	458	416	12	0	1721	1694	26	3	254	251	4	8	335	355	15	2	311	227
19	5	837	851	14	0	600	589	0	4	715	754	5	8	268	317	16	2	361	346
21	5	327	395	16	0	415	437	2	4	271	273	6	8	353	417	17	2	411	447
23	5	650	630	18	0	948	978	3	4	405	347	8	8	423	449	23	2	723	699
25	5	315	246	20	0	734	693	4	4	1173	1170	10	8	474	461	0	3	419	471
1	6	1355	1393	22	0	1111	1150	5	4	486	443	11	8	324	227	1	3	246	173
2	6	568	554	26	0	529	545	6	4	631	644	12	8	422	391	2	3	282	270
3	6	877	883	1	1	1178	1137	7	4	334	380	13	8	437	392	3	3	470	489
4	6	474	494	2	1	1152	1100	8	4	1233	1242	14	8	775	778	4	3	348	349
5	6	1297	1312	3	1	768	768	9	4	813	764	17	8	264	326	5	3	519	509
6	6	329	371	4	1	410	431	10	4	835	870	1	9	393	381	6	3	410	425
7	6	450	478	5	1	1739	1718	11	4	275	289	2	9	726	732	7	3	1101	1082
8	6	240	269	6	1	767	772	12	4	.31	757	3	9	426	464	8	3	466	448
9	6	919	907	7	1	404	378	14	4	1061	1051	4	9	270	242	9	3	289	286
10	6	415	354	8	1	524	572	15	4	424	360	5	9	354	329	10	3	648	617
12	6	264	280	9	1	1055	1016	16	4	385	409	6	9	628	572	11	3	918	933
13	6	748	742	10	1	508	548	17	4	388	382	8	9	265	244	14	3	646	663
14	6	310	311	11	1	244	248	18	4	776	790	9	9	408	345	15	3	609	608
16	6	340	317	12	1	516	494	20	4	296	222	10	9	380	353	17	3	275	175
17	6	989	1004	13	1	1092	1086	22	4	490	490	12	9	291	268	18	3	655	622
18	6	384	332	14	1	329	371	25	4	290	307	13	9	397	390	19	3	262	223
19	6	326	356	15	1	235	227	1	5	1341	1330	1	10	737	689	20	3	421	431
21	6	396	449	16	1	311	231	2	5	871	770	3	10	595	635	21	3	247	252
23	6	608	606	17	1	784	784	3	5	563	530	5	10	651	701	22	3	291	274
0	7	861	847	20	1	387	363	4	5	504	508	7	10	612	569	1	4	699	686
3	7	696	678	21	1	657	657	5	5	962	992	**L = 5****				2	4	957	974
4	7	792	740	22	1	410	425	6	5	746	760	2	0	1150	1201	3	4	218	213
5	7	439	435	24	1	626	655	7	5	570	553	4	0	1786	1687	4	4	477	468
6	7	375	398	25	1	360	375	8	5	297	311	6	0	1161	1146	6	4	1069	1103
7	7	656	641	26	1	474	438	9	5	562	571	8	0	1560	1529	7	4	473	503
8	7	942	970	27	1	458	407	10	5	1030	1066	10	0	1335	1293	8	4	964	968
9	7	586	587	0	2	349	355	12	5	577	616	12	0	631	626	9	4	369	341
10	7	238	222	1	2	916	865	13	5	538	564	14	0	693	714	10	4	547	558
12	7	503	457	2	2	518	552	14	5	599	564	16	0	444	416	11	4	449	452
13	7	274	284	3	2	1154	1098	15	5	394	316	18	0	764	702	12	4	889	898
14	7	470	450	4	2	627	644	16	5	598	600	20	0	878	881	13	4	646	660
18	7	680	647	5	2	515	471	17	5	561	545	22	0	473	500	14	4	601	600
19	7	528	517	6	2	932	911	18	5	345	292	24	0	847	788	15	4	293	271
1	8	375	422	7	2	618	624	19	5	368	314	26	0	292	357	16	4	782	786
2	8	630	636	8	2	644	624	20	5	275	291	0	1	522	525	19	4	258	271
4	8	482	463	11	2	1033	1072	21	5	803	805	1	1	354	333	20	4	470	464
5	8	387	381	12	2	545	548	23	5	300	331	2	1	540	543	21	4	265	325
6	8	330	319	13	2	559	573	24	5	387	425	3	1	1599	1574	0	5	638	648
7	8	572	560	14	2	265	250	0	6	624	655	4	1	725	732	1	5	870	890
8	8	543	519	15	2	781	786	1	6	1092	1144	5	1	205	174	3	5	947	969
9	8	358	314	16	2	237	232	2	6	482	458	6	1	840	815	4	5	551	580
12	8	599	623	17	2	454	485	3	6	1084	1107	7	1	1330	1334	5	5	240	253
13	8	516	541	18	2	440	398	4	6	485	476	8	1	677	677	6	5	452	391
15	8	604	545	19	2	294	338	5	6	401	377	9	1	370	334	7	5	703	691
16	8	681	656	21	2	518	529	6	6	364	404	10	1	651	650	8	5	1156	1143
19	8	354	376	24	2	321	256	7	6	1215	1178	11	1	813	793	9	5	414	441
0	9	537	558	25	2	780	815	11	6	700	651	12	1	283	265	10	5	765	722
1	9	586	600	27	2	242	161	14	6	290	301	13	1	202	197	11	5	366	392
4	9	654	713	1	3	184	166	15	6	589	629	14	1	286	276	12	5	990	991
5	9	485	467	3	3	297	231	18	6	313	335	15	1	680	666	14	5	608	572
7	9	374	365	4	3	354	303	19	6	723	768	18	1	263	240	15	5	520	507
8	9	609	641	5	3	1012	1006	20	6	310	287	19	1	693	689	16	5	290	270
11	9	611	564	6	3	764	786	21	6	507	516	21	1	280	263	17	5	261	207
12	9	345	292	7	3	206	208	22	6	274	293	22	1	521	494	18	5	450	416
13	9	364	330	8	3	280	320	1	7	517	503	23	1	506	503	19	5	659	655
14	9	357	285	9	3	1044	1006	2	7	954	932	24	1	529	525	22	5	334	315
15	9	618	610	10	3	932	915	5	7	600	604	25	1	501	536	1	6	916	907
1	10	736	724	11	3	273	313	6	7	822	821	26	1	700	721	2	6	882	908
2	10	344	302	12	3	934	937	7	7	420	394	1	2	906	911	3	6	538	524
3	10	634	624	13	3	965	962	8	7	451	409	2	2	409	372	4	6	358	258
5	10	676	711	14	3	223	223	9	7	385	385	4	2	882	865	5	6	1064	1057
7	10	346	354	16	3	957	970	10	7	463	455	5	2	984	957	9	6	827	818
9	10	863	866	17	3	590	587	11	7	374	374	6	2	497	500	10	6	550	556
L = 4**				18	3	391	422	12	7	425	480	7	2	407	387	13	6	514	506
0	0	1456	1436	19	3	378	381	16	7	703	679	8	2	263	238	14	6	241	183
2	0	776	811	20	3	577	606	17	7	449	467	9	2	904	901	17	6	723	689
4	0	1803	1793	21	3	393	300	20	7	625	629	11	2	394	397	18	6	410	426

Table 38 continued

H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL	H	K	FOBS	FCAL
**L =		5****		23	2	345	289	**L =		7****		0	5	594	598	5	3	265	250
19	6	316	308	1	3	457	445	2	0	1356	1417	1	5	453	496	7	3	404	395
2C	6	313	246	2	3	866	868	4	0	709	715	3	5	655	655	10	3	376	353
0	7	1306	1341	3	3	488	481	6	0	1034	1053	4	5	634	641	12	3	532	603
3	7	470	491	4	3	503	518	8	0	318	300	7	5	721	750	13	3	512	542
4	7	909	901	5	3	560	555	10	0	763	705	8	5	609	612	15	3	397	418
5	7	251	243	6	3	462	430	12	0	411	373	10	5	421	446	16	3	667	720
7	7	324	354	8	3	350	349	14	0	476	477	11	5	539	570	0	4	725	722
8	7	345	395	9	3	517	523	16	0	687	676	12	5	587	549	1	4	340	344
9	7	370	328	10	3	222	282	18	0	655	717	14	5	427	437	4	4	774	780
10	7	380	392	12	3	478	575	20	0	934	902	15	5	550	486	5	4	275	347
14	7	619	581	13	3	630	618	0	1	756	758	17	5	327	300	8	4	648	669
18	7	642	630	16	3	676	659	1	1	453	516	1	6	590	583	10	4	415	408
2	8	582	586	17	3	330	338	2	1	376	405	2	6	450	411	12	4	394	355
4	8	356	351	18	3	392	415	3	1	699	699	3	6	433	462	14	4	476	519
6	8	321	357	19	3	247	174	4	1	546	564	4	6	416	361	1	5	462	494
7	8	259	315	22	3	370	369	5	1	532	539	5	6	878	923	2	5	644	642
8	8	344	325	0	4	885	836	6	1	435	422	6	6	381	317	5	5	481	480
10	8	351	350	3	4	294	243	7	1	891	895	8	6	325	368	6	5	520	482
11	8	253	231	4	4	955	975	8	1	300	305	9	6	741	723	7	5	354	402
12	8	650	645	5	4	303	327	9	1	346	412	10	6	352	352	9	5	672	688
15	8	402	371	6	4	508	508	10	1	314	335	13	6	811	630	10	5	404	378
0	9	572	541	7	4	267	312	11	1	681	620	14	6	264	261	12	5	260	290
1	9	394	403	8	4	953	955	12	1	324	262	0	7	437	5C3	0	6	287	251
3	9	289	317	10	4	446	472	14	1	366	361	1	7	306	387	1	6	301	360
4	9	642	606	11	4	693	682	15	1	725	750	3	7	406	442	2	6	249	303
8	9	433	420	12	4	619	625	16	1	428	409	4	7	481	500	3	6	638	669
**L =		6****		14	4	821	799	18	1	636	640	5	7	365	365	7	6	740	731
0	0	2035	2008	15	4	306	284	19	1	598	610	6	7	395	378	8	6	372	384
2	0	563	596	18	4	674	709	21	1	415	370	7	7	305	233	**L =		9****	
4	0	1578	1551	19	4	298	308	1	2	276	309	8	7	403	370	2	0	1621	1564
6	0	1067	1077	1	5	706	746	3	2	290	300	9	7	258	249	4	0	453	393
8	0	561	569	2	5	646	646	4	2	556	575	10	7	405	388	6	0	722	809
10	0	783	788	3	5	263	254	5	2	554	528	2	8	659	702	8	0	496	521
12	0	662	680	5	5	1C78	1097	7	2	460	471	**L =		8****		10	0	571	534
14	0	585	548	6	5	860	800	9	2	902	911	0	0	1447	1466	12	0	411	448
16	0	768	830	8	5	502	491	10	2	338	324	2	0	297	330	0	1	479	490
18	0	482	451	9	5	667	670	12	2	338	285	4	0	1214	1194	1	1	663	682
20	0	645	600	10	5	940	938	13	2	892	934	8	0	726	759	2	1	326	332
22	0	945	985	12	5	647	637	14	2	363	373	12	0	552	573	3	1	491	474
24	0	352	319	13	5	300	293	15	2	571	593	14	0	527	540	4	1	403	447
1	1	817	781	14	5	659	667	16	2	550	476	16	0	336	325	5	1	604	610
2	1	812	794	16	5	461	445	17	2	668	717	18	0	591	572	6	1	467	420
3	1	462	432	17	5	605	607	19	2	628	579	1	1	379	405	7	1	507	522
4	1	764	756	20	5	414	397	21	2	450	485	2	1	531	520	8	1	317	321
5	1	1094	1109	0	6	871	890	0	3	433	378	3	1	706	680	9	1	406	388
6	1	611	633	1	6	649	622	1	3	422	426	4	1	470	467	11	1	583	565
7	1	347	321	3	6	980	953	3	3	448	478	5	1	586	583	12	1	326	291
8	1	759	762	4	6	430	426	4	3	330	365	7	1	719	738	3	2	339	339
9	1	823	847	5	6	375	357	5	3	496	511	8	1	297	350	4	2	328	316
10	1	439	379	6	6	361	358	6	3	495	459	9	1	677	669	5	2	626	587
12	1	320	330	7	6	963	958	7	3	389	373	12	1	418	384	6	2	354	376
13	1	777	747	8	6	270	223	8	3	447	438	13	1	679	692	7	2	291	291
14	1	392	396	11	6	653	675	10	3	232	188	14	1	252	171	9	2	544	526
17	1	728	72C	12	6	275	188	11	3	626	652	15	1	252	353	10	2	293	250
2C	1	392	438	15	6	628	608	13	3	336	392	16	1	600	606	1	3	600	550
21	1	492	482	16	6	426	444	14	3	943	926	17	1	660	661	3	3	456	498
22	1	289	305	1	7	362	341	15	3	519	543	1	2	280	225	4	3	316	283
23	1	453	423	2	7	901	923	17	3	401	359	2	2	416	415	5	3	335	403
24	1	527	535	4	7	351	350	18	3	442	466	3	2	242	319	8	3	354	388
1	2	449	466	5	7	460	418	19	3	425	423	5	2	440	417	10	3	303	286
3	2	960	980	6	7	728	710	20	3	400	370	6	2	305	320	11	3	301	295
4	2	440	469	7	7	262	274	2	4	862	888	7	2	429	419	2	4	659	672
6	2	287	215	9	7	277	294	6	4	725	773	8	2	363	389	5	4	286	290
7	2	982	961	12	7	368	353	7	4	376	398	11	2	743	749	6	4	743	745
8	2	361	312	13	7	251	203	8	4	268	298	12	2	389	320	1	5	318	281
11	2	920	941	15	7	323	314	9	4	295	304	13	2	572	585	**L =		10****	
14	2	327	369	0	8	842	878	10	4	598	571	14	2	359	394	0	0	813	853
15	2	694	689	4	8	634	592	12	4	599	527	15	2	895	914	4	0	862	830
18	2	316	240	5	8	364	316	13	4	258	253	17	2	776	809	1	1	521	514
19	2	344	369	9	8	287	359	14	4	531	499	1	3	440	370	2	1	519	494
2C	2	276	285	10	8	474	499	15	4	298	225	3	3	657	662	3	1	346	328
21	2	571	570	2	9	358	367	16	4	711	718	4	3	288	295				

Table 39

Atomic Coordinates and Isotropic Temperature Factors

Name	x	y	z	B*
Rh	0.11298(3)	0.12204(7)	-0.25000	2.25
Cℓ	0.0770(1)	0.0895(3)	-0.4336(4)	5.07
P1	0.12326(9)	-0.0662(2)	-0.2471(6)	2.28
P2	0.1655(1)	0.1689(3)	-0.1363(4)	2.39
P3	0.0729(1)	0.2767(3)	-0.2305(5)	2.61

* These values are equivalent isotropic temperature factors corresponding to the anisotropic temperature factors given in Table 40

Table 39 continued

(a) Phenyl Carbon Rigid Bodies

Name	x	y	z	B
C111	0.0719(2)	-0.1234(8)	-0.2267(7)	2.4(3)
C112	0.0441(3)	-0.0622(6)	-0.1603(9)	4.3(4)
C113	0.0055(3)	-0.1035(7)	-0.1377(8)	4.5(4)
C114	-0.0053(2)	-0.2059(8)	-0.1815(7)	4.6(4)
C115	0.0225(3)	-0.2671(6)	-0.2478(9)	4.7(3)
C116	0.0611(3)	-0.2258(7)	-0.2704(8)	3.1(3)
D	0.431(6)	$x^{1\ddagger}$	0.0333(2)	
E	0.374(7)	$y^{1\ddagger}$	-0.1646(5)	
F	0.412(6)	$z^{1\ddagger}$	-0.2041(6)	
C121	0.1444(3)	-0.1377(9)	-0.3768(7)	2.0(4)
C122	0.1535(3)	-0.2484(8)	-0.3710(8)	3.2(4)
C123	0.1722(3)	-0.2995(6)	-0.469(1)	5.6(5)
C124	0.1819(3)	-0.2400(9)	-0.5726(7)	4.6(5)
C125	0.1728(3)	-0.1293(8)	-0.5784(8)	4.4(4)
C126	0.1540(3)	-0.0782(6)	-0.481(1)	3.7(4)
D	6.065(6)	x^{1}	0.1631(2)	
E	1.162(6)	y^{1}	-0.1888(6)	
F	2.662(7)	z^{1}	-0.4747(6)	
C131	0.1510(5)	-0.1328(7)	-0.121(2)	2.1(4)
C132	0.1303(6)	-0.1529(7)	-0.0126(9)	3.0(4)
C133	0.1503(8)	-0.2012(7)	0.085(2)	4.0(4)
C134	0.1911(5)	-0.2294(7)	0.074(2)	4.0(4)

(Table continued)

Name	x	y	z	B
C135	0.2118(6)	-0.2093(7)	-0.0335(9)	3.0(3)
C136	0.1918(8)	-0.1611(7)	-0.131(2)	2.9(3)
D	5.154(5)	x^1	0.1710(2)	
E	0.66(1)	y^1	-0.1811(4)	
F	1.47(1)	z^1	-0.0231(6)	
C211	0.2107(3)	0.0905(6)	-0.183(3)	2.7(4)
C212	0.2409(8)	0.0560(9)	-0.104(1)	4.3(4)
C213	0.2751(6)	0.0026(8)	-0.149(2)	3.6(4)
C214	0.2790(3)	-0.0163(6)	-0.273(3)	3.5(4)
C215	0.2488(8)	0.0182(9)	-0.352(1)	6.1(5)
C216	0.2146(6)	0.0716(8)	-0.308(2)	4.3(5)
D	5.210(5)	x^1	0.2448(2)	
E	1.79(2)	y^1	0.0371(4)	
F	1.74(2)	z^1	-0.2281(8)	
C221	0.1842(3)	0.3102(6)	-0.164(1)	1.6(3)
C222	0.1737(3)	0.3948(9)	-0.0855(7)	3.1(3)
C223	0.1869(3)	0.5004(7)	-0.1094(9)	4.1(4)
C224	0.2106(3)	0.5214(6)	-0.212(1)	4.2(4)
C225	0.2211(3)	0.4368(9)	-0.2896(7)	5.5(5)
C226	0.2079(3)	0.3312(7)	-0.2657(9)	4.7(4)
D	3.311(6)	x^1	0.1974(2)	
E	0.996(5)	y^1	0.4158(5)	
F	1.906(6)	z^1	-0.1875(6)	

(Table continued)

Name	x	y	z	B
C231	0.1657(8)	0.1601(9)	0.0305(7)	2.9(3)
C232	0.1326(5)	0.1091(8)	0.084(2)	3.8(4)
C233	0.1292(4)	0.1059(7)	0.210(2)	5.7(5)
C234	0.1591(8)	0.1536(9)	0.2825(7)	6.9(5)
C235	0.1922(5)	0.2045(8)	0.229(2)	5.6(4)
C236	0.1955(4)	0.2078(7)	0.103(2)	4.2(4)
D	4.186(5)	x^1	0.1624(2)	
E	1.54(1)	y^1	0.1568(5)	
F	6.22(1)	z^1	0.1565(7)	
C311	0.0767(3)	0.3751(9)	-0.105(1)	2.8(4)
C312	0.0794(3)	0.3329(6)	0.012(1)	3.4(4)
C313	0.0834(3)	0.403(1)	0.1107(9)	5.4(4)
C314	0.0846(3)	0.5151(9)	0.092(1)	6.9(6)
C315	0.0819(3)	0.5573(6)	-0.025(1)	7.9(6)
C316	0.0779(3)	0.487(1)	-0.1235(9)	4.8(4)
D	3.183(6)	x^1	0.0806(2)	
E	1.658(7)	y^1	0.4451(6)	
F	0.665(8)	z^1	-0.0064(8)	
C321	0.0700(5)	0.3672(8)	-0.361(1)	3.4(4)
C322	0.0363(3)	0.432(1)	-0.384(1)	5.7(5)
C323	0.0366(3)	0.5048(8)	-0.4815(9)	6.0(5)
C324	0.0707(5)	0.5120(8)	-0.556(1)	5.0(5)
C325	0.1044(3)	0.447(1)	-0.533(1)	7.0(5)

(Table continued)

Name	x	y	z	B
C326	0.1040(3)	0.3743(8)	-0.4358(9)	4.6(4)
D	2.351(6)	x^1	0.0703(2)	
E	0.567(9)	y^1	0.4396(6)	
F	2.00(1)	z^1	-0.4586(7)	
C331	0.0202(3)	0.2307(7)	-0.212(4)	3.3(4)
C332	0.003(1)	0.2158(9)	-0.098(3)	4.4(4)
C333	-0.037(1)	0.175(1)	-0.089(1)	6.4(5)
C334	-0.0585(3)	0.1501(7)	-0.193(4)	5.9(5)
C335	-0.041(1)	0.1650(9)	-0.307(3)	11.3(8)
C336	-0.002(1)	0.205(1)	-0.316(1)	7.3(6)
D	1.203(5)	x^1	-0.0191(2)	
E	1.49(2)	y^1	0.1904(4)	
F	1.42(2)	z^1	-0.2027(7)	

‡ These values represent the ring centre of gravity coordinates

(Table continued)

(b)   Phenyl Hydrogen Rigid Bodies

Name	x	y	z	B
H112	0.051	0.011	-0.129	4.7
H113	-0.014	-0.060	-0.090	5.0
H114	-0.033	-0.236	-0.165	5.1
H115	0.015	-0.341	-0.279	5.2
H116	0.081	-0.270	-0.318	3.4
D	0.431			
E	0.374			
F	1.459			
H122	0.147	-0.291	-0.296	3.5
H123	0.179	-0.379	-0.464	6.1
H124	0.196	-0.277	-0.643	5.1
H125	0.180	-0.087	-0.653	5.9
H126	0.147	0.001	-0.485	4.1
D	6.065			
E	1.162			
F	3.709			
H132	0.101	-0.132	-0.005	3.3
H133	0.135	-0.215	0.162	4.4
H134	0.205	-0.264	0.144	4.4
H135	0.241	-0.230	-0.041	3.3
H136	0.207	-0.147	-0.208	3.2

(Table continued)

Name	x	y	z	B
D	5.154			
E	0.66			
F	2.51			
H212	0.238	0.070	−0.014	4.7
H213	0.297	−0.022	−0.091	4.0
H214	0.303	−0.055	−0.305	3.8
H215	0.252	0.005	−0.441	6.7
H216	0.193	0.097	−0.365	4.7
D	5.210			
E	1.79			
F	2.78			
H222	0.157	0.380	−0.012	3.4
H223	0.179	0.561	−0.053	4.5
H224	0.220	0.597	−0.229	4.6
H225	0.238	0.452	−0.363	6.1
H226	0.216	0.270	−0.322	5.2
D	3.311			
E	0.996			
F	2.953			
H232	0.111	0.075	0.033	4.2
H233	0.106	0.069	0.249	6.3
H234	0.157	0.151	0.373	7.6
H235	0.214	0.239	0.280	6.2

(Table continued)

Name	x	y	z	B
H236	0.219	0.245	0.064	4.6
D	4.186			
E	1.54			
F	0.99			
H312	0.079	0.252	0.025	3.7
H313	0.085	0.372	0.195	5.9
H314	0.087	0.565	0.164	7.6
H315	0.082	0.638	-0.037	8.7
H316	0.076	0.518	-0.207	5.3
D	3.183			
E	1.658			
F	1.712			
H322	0.012	0.427	-0.330	6.3
H323	0.012	0.552	-0.498	6.6
H324	0.071	0.564	-0.626	5.5
H325	0.129	0.452	-0.587	7.7
H326	0.128	0.327	-0.420	5.1
D	2.351			
E	0.567			
F	3.047			
H332	0.018	0.234	-0.023	4.9
H333	-0.049	0.165	-0.007	7.1
H334	-0.087	0.121	-0.186	6.5

(Table continued)

Name	x	y	z	B
H335	-0.057	0.147	-0.382	12.4
H336	0.011	0.216	-0.398	8.1
D	1.203			
E	1.49			
F	2.46			

Table 40

Anisotropic Temperature Factors ($\mathring{A}^2 \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	29.6(5)	25.0(5)	31.0(6)	1.1(6)	$-$ 5(1)	$-$ 3(1)
Cl	75(3)	53(3)	64(3)	13(2)	$-$43(3)	$-$13(3)
P1	28(2)	28(2)	30(2)	0(1)	$-$ 1(3)	$-$ 5(5)
P2	32(2)	27(2)	32(3)	2(2)	0(2)	$-$ 2(2)
P3	35(2)	32(2)	32(3)	2(2)	3(3)	1(3)

Table 41

Selected Interatomic Distances

Atom 1	Atom 2	Distance (Å)	
Rh	Cℓ	2.376(4)	2.398(4)*
Rh	P1	2.334(3)	2.334(3)*
Rh	P2	2.214(4)	2.214(4)*
Rh	P3	2.322(4)	2.324(4)*
P1	C111	1.842(6)	
P1	C121	1.815(9)	
P1	C131	1.859(8)	
P2	C211	1.847(7)	
P2	C221	1.864(7)	
P2	C231	1.839(9)	
P3	C311	1.837(9)	
P3	C321	1.820(9)	
P3	C331	1.838(8)	

* Value corrected for riding

Table 42

Selected Intramolecular Angles

Atom 1	Atom 2	Atom 3	Angle (°)
P1	Rh	P2	97.9(2)
P1	Rh	P3	152.8(1)
P1	Rh	Cℓ	85.2(2)
P1	Rh	H112	67.2
P2	Rh	P3	100.4(1)
P2	Rh	Cℓ	156.2(2)
P2	Rh	H112	115.1
P3	Rh	Cℓ	86.1(2)
P3	Rh	H112	86.7
Cℓ	Rh	H112	88.0
P1	C111	C114	176.6(7)
P1	C121	C124	176.0(6)
P1	C131	C134	178.2(6)
P2	C211	C214	174.9(7)
P2	C221	C224	178.1(6)
P2	C231	C234	175.0(7)
P3	C311	C314	176.7(8)
P3	C321	C324	176.0(7)
P3	C331	C334	176.4(7)
Rh	P1	C111	104.3(3)
Rh	P1	C121	121.5(4)
Rh	P1	C131	121.1(4)

(Table continued)

Atom 1	Atom 2	Atom 3	Angle (°)
Rh	P2	C211	109.7(4)
Rh	P2	C221	114.1(3)
Rh	P2	C231	123.5(4)
Rh	P3	C311	124.7(4)
Rh	P3	C321	117.1(4)
Rh	P3	C331	107.2(3)
C111	P1	C121	105.3(5)
C111	P1	C131	101.2(5)
C121	P1	C131	100.8(4)
C211	P2	C221	100.0(4)
C211	P2	C231	104.3(6)
C221	P2	C231	102.4(5)
C311	P3	C321	101.3(5)
C311	P3	C331	100.4(5)
C321	P3	C331	103.0(5)

Table 43

Selected Intramolecular Non-bonded Contacts

Atom 1	Atom 2	Distance (Å)
Rh	H112	2.77
Rh	H216	2.94
Cℓ	H126	2.62
Cℓ	H336	2.70
H116	H122	2.18
H126	H216	2.31
H212	H236	2.39
H216	H226	2.31
H312	H332	2.07
C111	H132	2.62
C112	H132	2.68
C122	H116	2.47
C211	H226	2.69
C216	H226	2.44
C231	H212	2.68
C232	H312	2.59
C236	H212	2.55
C312	H332	2.38
C312	H222	2.62
C321	H316	2.51
C322	H316	2.56
C111	C121	2.91(1)

(Table continued)

Atom 1	Atom 2	Distance (Å)
C111	C131	2.86(1)
C121	C131	2.83(1)
C211	C221	2.84(1)
C211	C231	2.91(1)
C221	C231	2.83(1)
C311	C321	2.82(1)
C311	C331	2.82(1)
C321	C331	2.86(1)
C126	C216	3.32(1)
C131	C211	3.44(1)
C132	C232	3.38(1)
C135	C212	3.48(1)
C136	C211	3.20(1)
C136	C212	3.13(1)
C136	C213	3.40(1)
C222	C312	3.37(1)
C222	C316	3.36(1)
P1	P2	3.430(5)
P2	P3	3.485(5)
P1	Cℓ	3.208(6)
P3	Cℓ	3.190(6)

Table 44

Selected Intermolecular Contacts

Atom 1	Atom 2	Symmetry Operation (on atom 2)	Distance (Å)
Cℓ	H113	$\bar{x}$, $\bar{y}$, 1/2+z-1	2.71
H123	H213	1/2-x, 1/2+y-1, 1/2+z-1	2.38
H124	H134	x, y, z-1	2.37
H126	H234	x, y, z-1	2.43
H132	H335	$\bar{x}$, $\bar{y}$, 1/2+z	2.00
H212	H225	1/2-x, 1/2+y-1, 1/2+z	2.34
H213	H325	1/2-x, 1/2+y-1, 1/2+z	2.47

Fig. 14

A General View of the Red Form of RhCl(P(C$_6$H$_5$)$_3$)$_3$
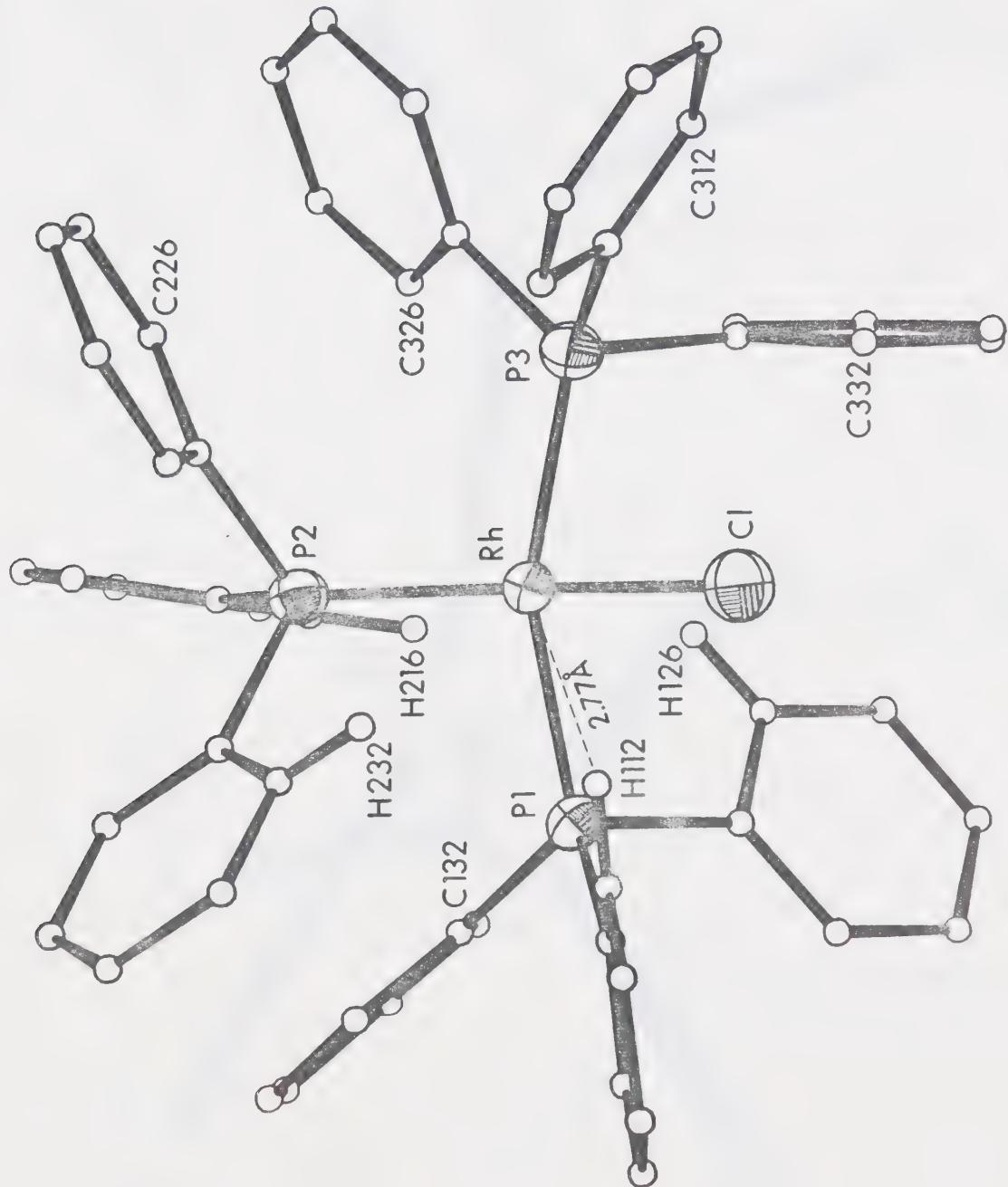
Fig. 15

Central Geometry Viewed down the P1-P3 Direction
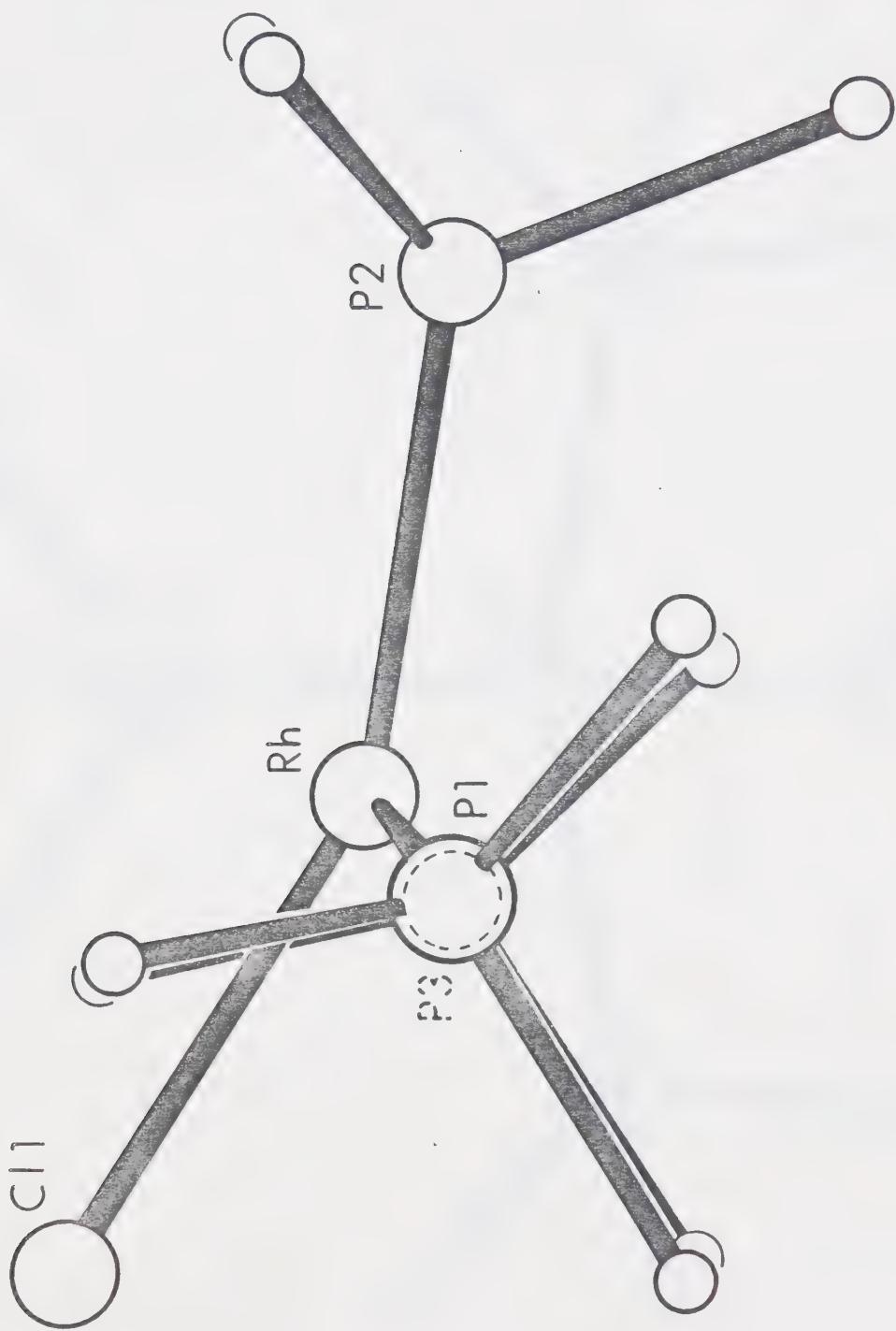
Fig. 16

View Perpendicular to the P1-P2-P3 Plane
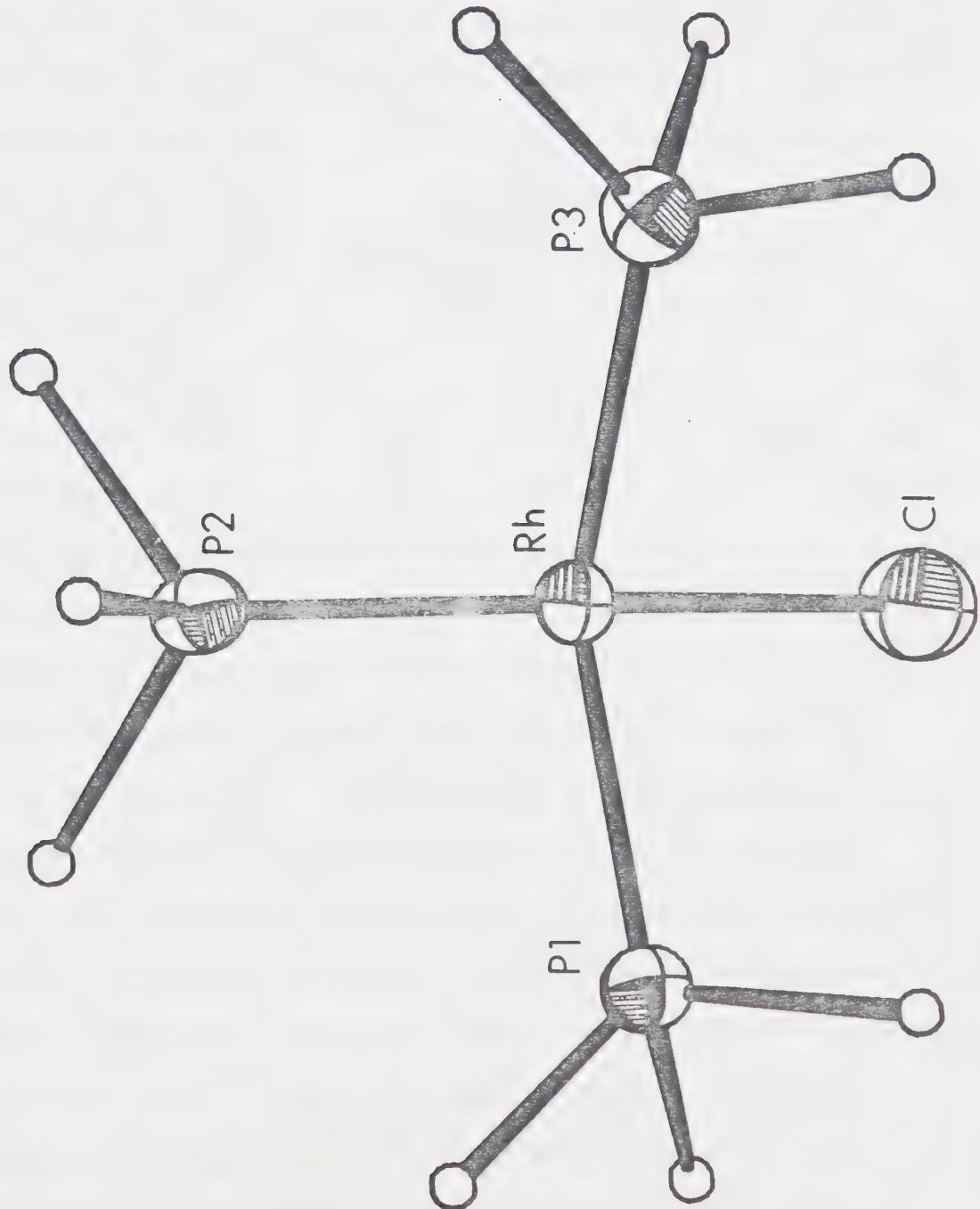
Discussion

The molecular structure of $RhCl(P(C_6H_5)_3)_3$ in the red crystalline modification is shown in Fig. 14. Simplified views of the central portion of the molecule are given in Figs. 15 and 16. These diagrams should be compared with Figs. 11, 12 and 13 to observe the major differences and similarities between the molecular structure in the red and orange allotropes. To a first approximation the rhodium coordination is square planar but a pronounced distortion towards a tetrahedral geometry is evident in Fig. 15. This distortion is greater than that observed for the orange modification as is clearly indicated by a comparison of Cl-Rh-P2 angles - 156.2(2)° (red) and 166.7(2)° (orange) - and P1-Rh-P3 angles - 152.8(1)° (red) and 159.1(2)° (orange). The actual deviations from planarity for the $RhClP_3$ fragment are given in Table 45. The magnitude of the distortion in the red form is sufficiently great that the only significant interligand repulsions occur between ligands directly bonded to rhodium. Both forms distort from the planar geometry in the same way i.e. towards a tetrahedral geometry. This should be compared with a pyramidal distortion observed in RhLCl (where L is the tridentate phosphine ligand $(C_6H_5)P((C_3H_6)P(C_6H_5)_2)_2$ [140].

Table 45

Weighted Mean Molecular Planes for $RhCl(P(C_6H_5)_3)_3$ [a]

Atoms Contained in the Planes	Modification	Equation
Rh, Cl, P1, P2, P3	red	$-0.6629X - 0.2857Y + 0.2690Z = -4.8112$
.. ..	orange	$-0.1624X + 0.1708Y + 0.9718Z = 4.2984$

Distances of Atoms from Planes

Atom	Distance (Å)	
	red	orange
Rh	0.010	-0.014
Cl	-0.489	-0.290
P1	0.469	0.419
P2	-0.436	-0.276
P3	0.492	0.234

a The orthogonal coordinate system (X,Y,Z) corresponds to the crystal abc axes.

It should be noted that the orange form is meta-
stable and converts to the red form on prolonged reflux
during the preparation. The methods of preparation of
the two forms differ only in the nature of the excess
reagent (see Chapter II and references therein). The red
form is prepared by slow addition of triphenylphosphine
to 'rhodium trichloride' i.e. the rhodium trichloride is
normally in excess, whereas the orange form is prepared
such that triphenylphosphine is the excess reagent. The
difference is then kinetic and suggests that the immediate
precursors to the forms of $RhC\ell(P(C_6H_5)_3)_3$ are different
and dependent on the reaction conditions. In the orange
form the product is not produced in its ground state.
It could thus be temporarily locked [119] in the metastable
geometry by the particular arrangement of the triphenyl-
phosphine groups.

The rhodium-ligand distances (uncorrected for
thermal motion) of this study, the equivalent values
reported by Mason *et al.*,[138,140] and the relevant data on
RhLCℓ are compared in Table 46.

The two determinations of the red form are in
excellent agreement and no significant deviations can be
detected. For the red form the rhodium-phosphorus bond
lengths to the chemically equivalent phosphorus atoms

Table 46

Distances (in Å) from Structures Containing the

RhClP$_3$ Fragment

	RhClP$_3$'[a] (red)	RhClP$_3$'[a] (red)[c]	(orange)	RhLCl
Rh-Cl	2.376(4)	2.386	2.404(4)	2.381(2)
Rh-P (P *trans* to Cl)	2.214(4)	2.210	2.225(4)	2.201(2)
Rh-P	2.322(4)	2.320	2.304(4)	2.288(2)
(P *trans* to P)	2.334(4)	2.331	2.338(4)	2.288(2)[b]
ΣRh-ligand	9.246	9.244	9.271	9.158
ΣRh-P	6.870	6.861	6.867	6.777
	this work	(138,140)	Chap. V	(140)

[a] P' represents triphenylphosphine

[b] related by symmetry to the value above

[c] most recent values for this work are available as a private communication in ref. 140

(P1 and P3) are the same within experimental error in contrast to an apparently significant difference in the orange form. In all four structure determinations the chemically unique rhodium-phosphorus bond is substantially shorter than the other two. As mentioned in

Chapter V this extreme shortening may be attributed to
significant π-acidity of triphenylphosphine. The complex
RhLCℓ shows considerably shorter rhodium-phosphorus dis-
tances than RhCℓ$(P(C_6H_5)_3)_3$.

In RhCℓ$(P(C_6H_5)_3)_3$, (red form), the rhodium
atom has one particularly close contact [142] with an *ortho*
hydrogen of the 11 phenyl group. This contact (Rh-H112,
2.77 Å) is apparently caused by repulsions involving atoms
on the opposite side of the phenyl group (Table 43). No
attractive character is attached to this contact. It
should be noted that the short contacts in the orange form
and RhLCℓ involve phenyls attached to the chemically
unique phosphorus and correspond to H216 in Fig. 14.

There appears to be a significant difference
($\Delta/\sigma \sim 4$) between the rhodium-chlorine bond lengths
observed in the red (2.376(4) Å) and the orange (2.404(4)
Å) forms. This difference persists even when the bond
lengths are modified for the effects of thermal motion.
This variation could be the result of the greater inter-
ligand repulsions which are present in the orange crystals
and it is reasonable that the effect should be noticeable
in the weaker rhodium-chlorine bond rather than the rhodium-
phosphorus bonds. Although the rhodium-phosphorus and rhodium
-chlorine bond lengths support this view the difference may
simply be an artifact of the data and thus not significant.

The geometry of the triphenylphosphine ligands
is normal with respect to the angles C-P-C and Rh-P-C
(Table 42):   C-P-C, free ligand ~ 103°;[129] complexed
ligand ~ 102°; Rh-P-C ~ 115°. However the geometry is
abnormal with respect to the phosphorus-carbon distances.
The average of the six-phosphorus-carbon distances invol-
ving Pl and P3 is 1.835 Å whereas the other three dis-
tances involving P2 average 1.850 Å cf. 1.828 Å for the
free ligand. No comparable trend is reported in RhLCl.
In fact in this molecule there is no apparent difference
between P-C (sp^2) and P-C (sp^3) which has been observed
in other phosphine complexes where the phosphorus is
attached to aryl or alkyl substituents[143]. The com-
parable values for the orange form were 1.838 Å and
1.855 Å respectively. Combining the data from the two
modifications gives mean phosphorus-carbon bond lengths
of 1.837(4) Å and 1.852(5) Å for the two types of tri-
phenylphosphine ligands. By normal crystallographic
standards the phosphorus-carbon bonds of the phosphine
trans to the chlorine atom are significantly larger than
normal (Δ/σ ~ 4) while no convincing difference is
observed between the phosphorus-carbon distances of the
mutually *trans* phosphines, typical literature values[17,18,129]
and the average phosphorus-carbon bond distance (1.827(9) Å)

observed in the dioxygen derivatives as mentioned in
Chapters III and IV.

It would be pleasing if the extremely short
rhodium-phosphorus bond, the lengthening of the associated
phosphorus-carbon bonds and π-bonding could be related in
a simple manner. Arguments using covalent radii for
spherical atoms, to explain metal-phosphorus distances
are tenuous since the geometry about the phosphorus atom
is far from tetrahedral [143] and an anisotropy of covalent
radius is expected as a result of the different mixtures
of 's' and 'p' character in the various bonds [144]. Since
the 3s and 3p orbitals have distinctly different radii [145]
then σ-bonding alone would predict short metal-phosphorus
and long phosphorus-carbon bond lengths when compared to
values based on a simple covalent radius ($r_{sp}3$) for
phosphorus. As mentioned the angular properties of the
coordinated triphenylphosphine are essentially the same
as the free ligand so such a description cannot explain
the phosphorus-carbon distance variation. The difference
could be explained by greater participation of phosphorus
3d orbitals in the phosphorus-carbon σ-bonding, if the
argument concerning the differences in radial properties
of the phosphine atomic wave functions is extended to
include these orbitals.

The π-acidity of phosphine ligands involves phosphorus 3d orbitals and the σ and π components of the bonding are not separable in this case, thus the 3d orbitals should also participate in σ-bonding. The lengthening of the phosphorus-carbon bonds should then be related to the extremely short rhodium-phosphorus bond and π-bonding.

While this explanation may look plausible certain conflicting evidence does exist particularly in the structure of RhLCℓ which should show very similar features to $RhCℓ(P(C_6H_5)_3)_3$ with differences due to the constraints of the tridentate phosphine ligand. As indicated previously the long phosphorus-carbon bonds do not exist in this structure. The explanation is then either incomplete or incorrect. The probability of an error of this magnitude and direction (0.02 Å too long) in any of the structures under consideration seems low. There is a difference in the nature of the inductive effects [146] of the substituents of the chemically unique phosphorus atoms in these structures. In $RhCℓ(P(C_6H_5)_3)_3$ the three substituents are electron withdrawing phenyl groups whereas there is only one electron withdrawing phenyl group and two electron donating aliphatic chains in RhLCℓ. Thus the observed phosphorus-carbon bond lengthening might be very specific to triarylphosphines in an extensive π-

bonding situation. Considerably more data are required to solve this problem.

Finally the structural trends of $RhClP_3'$ and its derivatives can be analysed. The molecules fall into two classifications: (a) coordinatively unsaturated - $RhClP_3'$, $RhCl(P_2'(CS)$, $RhClP_2'(C_2F_4)$, (b) coordinatively saturated - $(O_2)RhClP_3'$, $[(O_2^-)RhClP_2']_2$. The trends corresponding to ligand replacement within each group can be analysed and then trends associated with ligand addition can be deduced. The three species present in group (a) contain a common structural fragment $RhClP_2'$ with the only differences being due to the ligand *trans* to the chlorine atom. The data for these complexes are summarised in Table 47. These data show a small range of rhodium-chlorine distances (the value 2.404(4) $\overset{\circ}{A}$ for the orange form of $RhCl(P(C_6H_5)_3)_3$ should probably be excluded from the comparison for reasons cited earlier). The significant changes in the rhodium-phosphorus bond lengths *cis* to the chlorine atom must then reflect changes in rhodium-phosphorus π-bonding [141] and the ligands can be arranged in order of π-acidity - $C_2F_4 > CS > P(C_6H_5)_3$.

Table 47

Ligand *trans* to Cl	Rh-Cl (Å)	Rh-P (*trans* to P) (Å)		Ref.
P(C$_6$H$_5$)$_3$(red)	2.376(4)	2.328	2.334(3) 2.322(4)	This work
P(C$_6$H$_5$)$_3$(red)	2.386	2.326	2.320 2.331	138,140
P(C$_6$H$_5$)$_3$(orange)	2.404(4)	2.321	2.304(4) 2.338(4)	Chap. V
CS	2.386(3)	2.336	2.335(2) 2.337(2)	121
C$_2$F$_4$	2.375(8)	2.372	2.374(8) 2.370(8)	138

The group (b) compounds are compared in Table 48. The common structural fragment is O$_2$RhClP$_3'$. The geometry of these complexes can be treated as trigonal bipyramidal and the differences occur in an axial position. Within this series the rhodium-chlorine distances are effectively constant. The greatest changes occur in both the axial and equatorial rhodium-phosphorus distances. In the *tris*-phosphine complex these distances are longer by approximately 0.06 Å and 0.08 Å respectively. This difference must be mainly due to the different axial ligands P' and O2'. The oxygen in the axial position has no

Table 48

	$O_2RhClP'_3$ Distance (Å)		$[O_2RhClP'_2]_2$ Distance (Å)	
equatorial				
Rh-Cl	2.391(3)		2.390(3)	
Rh-P	2.357(3)		2.277(3)	
Rh-O_2	2.043[a]	$\begin{cases} 2.081(8) \\ 2.005(8) \end{cases}$	2.090[a]	$\begin{cases} 2.198(7) \\ 1.983(7) \end{cases}$
axial				
Rh-P	2.375[a]	$\begin{cases} 2.362(4) \\ 2.387(4) \end{cases}$	2.314(3)	
5th other ligand	P'		O2'	

a - average of two distances.

vacant orbitals in a suitable geometry to accept π-electrons from the rhodium. Thus in $O_2RhClP'_3$ there are four ligands (3P' and O_2) competing for π-electron density whereas in the half unit of $[O_2RhClP'_2]_2$ there are only three ligands (2P' and O_2) and it would be reasonable to expect the observed trend but not perhaps the magnitude. The average rhodium-oxygen distance is greater in the dimeric species than in the monomeric *tris*-phosphine

complex. However while the average is higher one dis-
tance is short (1.983(7) Å) and the other very long
(2.198(7) Å). While it is difficult to assess how much
of this assymmetry is due to the nature of the bridge in
the dimer the difference parallels the trend observed in
$O_2RhC\ell P_3'$. In this latter case the rhodium-oxygen (O
pseudo *trans* to P) distance was significantly longer than
the rhodium-oxygen distance involving O pseudo *trans* to
Cℓ. In the dimeric species the magnitude of the dif-
ference is much greater. In discussions of the '*trans*'
effect it is convenient to view the molecules as having
a distorted octahedral geometry (i.e. each oxygen occupies
a separate site rather than O_2 occupying a single coordin-
ation site). If the '*trans*' effect is modified by the
extent of π-bonding [139,141] and the difference in rhodium-
phosphorus bond lengths ($O_2RhC\ell P_3'$ to $[O_2RhC\ell P_2']_2$) reflects
an increase in the π-bonding, then a more marked assym-
metry for the bound dioxygen in $[O_2RhC\ell P_2']_2$ would be ex-
pected regardless of the constraints due to bridge for-
mation.

The changes in geometry that accompany the
chemical reaction:

$$RhC\ell P_3' + O_2 \rightarrow O_2RhC\ell P_3'$$

can be summarised as follows:

(1) An oxygen molecule can be expected to approach an open site of $RhClP_3'$ to form a square pyramidal inter-mediate which transforms to a trigonal bipyramidal struc-ture by normal angular deformation. This is supported by the only major angular changes upon oxygenation being within the equatorial plane ligands (see Tables 12, 22, 32, and 42).

(2) The rhodium-phosphorus bond lengths increase.

(3) No change in rhodium-chlorine distances.

The constancy of the rhodium-chlorine distances throughout the series and the variation in rhodium-phosphorus bond lengths supports the concepts of π-bonding for the ligands P' and O_2. Electro neutrality for the rhodium atom is then achieved by variations in the π-bonding components.

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Appendix 1

Programmes Used

Author	Title	Description
D.P. Shoemaker	MIXG2	Calculates Picker diffractometer settings
M.J. Bennett	PMMO	Calculates intensities, makes LP corrections for Picker data
M. Elder	D-refine	Refines axial lengths (modified by K. Simpson)
A. Zalkin	FORDAP	Fourier summation for Patterson or electron density maps
M.J. Bennett	MMMR	Calculates starting parameters for rigid bodies or hindered rotors.
W.C. Hamilton	GONO9	Absorption correction calculator
C.T. Prewitt	BURP	Enlarged version of SFLS5HR structure factor calculation and least squares refinement (modified by B. Foxman and W. Brooks)
G.J. Williams	CROMERS	Calculates form factors curves from Cromer's coefficients
J.S. Wood	MGEOM	Calculates bond lengths, angles and best planes

W. Busing and H.A. Levy	ORFFE II	Calculates bond lengths, angles and associated errors (modified by B. Penfold, W.L. Brooks and M. Elder)
C. Johnson	ORTEP	Writes plot command tape for Calcomp plotter
M. Cowie	PUBE	Sorts reflection data according to any desired hkℓ sequence
R.C. Elder	PUBTAB	Tabulates reflection data for publication (modified by M. Cowie)

All programmes were run using an IBM 360 model 67 computer.

Appendix 2

Conventional Crystallographic Symbols

as Defined in Vol. I, Page xi, of the

International Tables for

X-ray Crystallography

h,k,ℓ	indices of the reflection from a set of parallel planes
a,b,c	lengths of unit cell edges
α, β, γ	interaxial angles
a*, b*, c*	lengths of reciprocal unit cell edges
$\alpha*, \beta*, \gamma*$	interaxial angles in reciprocal space
$x_i, y_i, z_i,$	fractional coordinates of an atom i in units of a,b,c
$F_{hk\ell}$	structure factor for the unit cell, corresponding to the Bragg reflection hkℓ.
$\bar{u}^2$	mean square amplitude of atomic vibration
B	Debye isotropic thermal parameter; $B = 8\pi^2\bar{u}^2$
$U_{11}, U_{22}, U_{33},$	anisotropic thermal parameters used to describe ellipsoidal electron distribution of the anisotropically vibrating atom; the temperature factor expression is then: $\exp[-2\pi^2(U_{11}h^2a*^2 + U_{22}b^2B*^2 + U_{33}\ell^2c*^2 + 2U_{12}hka*b* \cos\gamma* + 2U_{13}h\ell a*c*\cos\beta* + 2U_{23}k\ell b*c* \cos\alpha*)]$
F_o	observed structure factors
F_c	calculated structure factors